CARBONIFEROUS ROCKS OF THE EASTERN AND CENTRAL MIDLAND VALLEY OF SCOTLAND : ORGANIC PETROLOGY, ORGANIC GEOCHEMISTRY AND EFFECTS OF IGNEOUS ACTIVITY.

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ABSTRACT

An integrated organic petrological and geochemical approach has been adopted to evaluate the variation in the type of organic materials contributing to the Carboniferous succession in the eastern and central Midland Valley and to assess the extent to which both extrusive and intrusive igneous activity have modified the optical and geochemical properties of organic matter in this province.

The type investigation reveals that the succession is extremely rich in organic matter, much of which originated from the vascular tissues of higher plants. The profound influence of terrestrial sedimentation throughout the Carboniferous is evident from the marked terrestrial overprinting of many known marine horizons. Much of the accumulated organic matter has been subjected to varying degrees of microbial reworking.

In addition to the characterisation of organic matter in oil shales (lamosites and torbanitic shales), humic coals, sapropelic coals, marine bands and carbonaceous clasts incorporated in volcanic vent deposits, each of which bear different petrological and/or geochemical signatures, a detailed evaluation was undertaken of the Lower Carboniferous (Viséan) sequence in east Fife, since the algal-rich shales in the Viséan have long been considered as the most likely source rocks for the oil shows and modest petroleum accumulations which occur in the Midland Valley. Although many of the oils and bitumens studied have suffered varying degrees of biodegradation and/or water washing, these early suspicions have been confirmed by the close correspondence between the biomarker profiles of the oils/bitumens studied and those of the non-marine, lamositic shales of the Lothians Oil-Shale Group (Lothians oil shales). Notwithstanding the close spatial relationship which exists between oil shows and igneous materials in many areas of the Midland Valley, a high-temperature origin for all of these hydrocarbons need not be invoked because consideration of regional maturation levels indicates that the Lower Carboniferous succession attained maturities conducive to the generation of liquid (and gaseous) hydrocarbons through the "conventional" course of burial metamorphism by the end of the Carboniferous period.

For the rank investigation, maturation profiles (based on vitrinite reflectance) for nearly forty boreholes and field sections in the Midland Valley were constructed and rank maps were prepared for different horizons throughout the Carboniferous. Lateral and vertical patterns of paleaoheatflow were monitored both before and after the intrusion of the Midland Valley Sill. The higher regional levels of organic maturation recorded in the west of the Midland Valley, at all levels in the Carboniferous, correspond to an increased thickness of the volcanic pile in the central and western parts of the province, suggesting that a greater regional heat sink existed in the west during the Carboniferous.

The optical and textural properties of vitrinite have been used to constrain the timing of sill emplacement with respect to the imposition of regional levels of coalification, from which deductions have been made about the importance of igneous activity in modifying background maturation profiles, not only in the Midland Valley, but elsewhere in the world. The early Permian tholeiitic Midland Valley Sill, which underlies most of the eastern and central Midland Valley, has caused the development of extensive thermal aureoles, in marked contrast to the preceding Lower to mid-Carboniferous alkaline-dolerite intrusions which have failed to induce any widespread alteration of organic matter. This major difference in organic-matter response is explained in terms of differing rank levels of organic matter at the time of intrusion and to differences in the degree of sediment compaction and water saturation, factors which probably also strongly influenced the rank level of organic matter prior to invasion by magmas.

Maturation of organic matter closely associated with extensive Surtseyan-type volcanicity in the eastern part of the Midland Valley displays no relationship to the regionally developed coalification in associated sediments. Maturation levels of clasts in pyroclastic vent deposits have generally not been raised much above the regional reflectance level, suggesting the incorporation of organic matter in ash streams in which water was an important coolant and protective agent.

The effects that different heating rates have had on commonly used molecular-maturity indices, based on both saturated and aromatic hydrocarbons, in different types of organic matter were also investigated. Results show that molecular-maturity parameters may significantly underestimate the maturities of samples in which the organic matter has experienced high rates of heating, either through igneous activity or a high background geothermal gradient, and that distinct "reversals" occur in many ratios at elevated ranks. Type influences are inferred for Tm/Ts and hopane/moretane ratios and for parameters based on distributions of methylphenanthrene isomers. Anomalous assessments of sample maturity may additionally derive from the lowering (suppression) of vitrinite reflectance which invariably occurs in samples containing abundant liptinitic materials, principally sporinite in the Carboniferous of the Midland Valley.

The results presented in this thesis carry important implications for hydrocarbon exploration. Accurate appraisals will only be achieved through the complete integration of organic petrological, geochemical and geological data in sedimentary sequences containing abundant hydrogen-prone organic components and/or in basins in which there has been widespread igneous activity.

CONTENTS

2. ORGANIC MATTER IN COALS AND SEDIMENTS

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GENERAL INTRODUCTION

The Midland Valley of Scotland is the term given to the NE-SW-trending geological province that is bounded by the Highland Boundary Fault to the north and the Southern Uplands Fault to the south. The general structure is that of an ancient graben, interposed between the metamorphosed Dalradian Highlands, lying at its northern margin, and the Palaeozoic trench sequence of the Southern Uplands which abuts to the south.

The area has had a long and complex geological history which saw the accumulation of more than 15km of mainly Devonian and Carboniferous sediments. The Devonian sediments are largely continental red sandstones and conglomerates representing deposition in a molasse-type basin. Carboniferous sedimention was more varied and proceeded under both lacustrine and fluvio-deltaic regimes which were punctuated by occasional marine incursions. Sediment deposition throughout the Palaeozoic was frequently interrupted by intrusive and extrusive igneous episodes of varying duration which, in conjunction with faulting, exerted a profound control on subsequent patterns of sedimentation. Post-Palaeozoic solid rocks are not represented in the graben and it is still uncertain as to whether this has arisen through non-deposition, erosion or a combination of both.

The diversity of lithologies and structural styles displayed within the Midland Valley has long been known to geologists and, not surprisingly, many fundamental geological principles and phenomena have been formulated and described, respectively, from outcrops in the area by such eminent pioneers as Hutton and Geikie.

Inevitably perhaps, economic considerations preceded any formal geological investigations and understanding, even though the processes leading to the formation of viable deposits were not recognised for some considerable time after their discovery. The exploitation of organic-rich materials predated that of other resources (notably minerals), with records of coal extraction dating back to the twelfth century. It was not until the mid-eighteenth century, however, that coal mining became a major industrial concern, only ever to be rivalled by the oil-shale industry which commenced in 1851 following the discovery of the Boghead Coal (torbanite) in Westphalian strata at Torbanehill, near Bathgate. Dinantian oil shales, cannel coals and canneloid shales were later used as raw materials in the retorting process.

In addition to the industrially-produced oils, natural seepages of hydrocarbons such as that occurring at St.Catherine's Well, Liberton, Edinburgh, have been known in the Midland Valley for centuries. Frequent observations of oil seeps in mines working the Dinantian oil shales provided perhaps the first evidence that these deposits could act as potential sources for natural petroleum accumulations.

Furthermore, the close association often noted between petroliferous deposits and igneous rocks (mainly intrusives) gave rise to the suggestion that many hydrocarbon shows seen within the Carboniferous strata could have arisen from the destructive distillation of oil shales through heat generated by the invading igneous material.

In many instances, however, hydrocarbon occurrences were noted in areas devoid of igneous activity, the most notable of these being the D'Arcy-Cousland anticline, bordering the Midlothian Coalfield, in which oil reservoirs were penetrated during exploratory drilling in the early part of the century. This discovery added to the increasing suspicion that many hydrocarbon accumulations could have their origins as "natural" petroleums *sensu stricto*, rather than as high-temperature igneous distillates. Further drilling in the 1930s and 1940s yielded numerous oil and gas shows at various horizons throughout the Carboniferous succession, but apart from the pumping of gas from the Cousland-1 well into the gasworks at Musselburgh, hydrocarbons were never present in sufficient quantity, or proved to be too difficult to extract, to warrant any large-scale production.

The increasing cost of offshore exploration over the past few years has promoted renewed geological interest in the sedimentary facies and structures which are likely to be conducive to the sourcing and trapping of hydrocarbons within the Midland Valley. Recent drilling on the flanks of the Midlothian Coalfield has resulted in the discovery of hydrocarbons within the Carrington-1 well, whilst the most notable success has been the penetration of several oil-bearing sandstone intervals in the Milton of Balgonie-1 borehole, located on the Balfour Anticline in central Fife. As in previous years, the main targets are the high-porosity, fluvio-deltaic, sandstones which provide ideal reservoir horizons for hydrocarbons generated from the organic-rich Dinantian shales, which have always been assumed to be the most likely source rocks.

Despite the long history of economic exploitation of fossil fuels in the Midland Valley, there is surprisingly little published data dealing with the nature, origin and mode of occurrence of organic matter, not only in coals and oil shales, but within the Carboniferous sequence generally. The development of the oil-shale industry provided the initial incentive for the study of organic-rich sediments, but petrological studies were confined to the description of thin sections viewed in transmitted light. The major drawback of this method, particularly with respect to oil-shale analysis, is its failure to resolve adequately the hydrogen-rich components (the main constituents of the oil shales) from each other and from the mineral matrix. These optical problems undoubtedly contributed to the many conflicting identifications of organic moieties in these sediments, which are

recorded in the early literature, and which were to be overcome through the use of reflected-light, oil immersion systems that radically enhanced the image and improved the contrast between the organic components. The later development of fluorescence microscopy was a further significant advance, enabling the rapid delineation of oil-prone organic matter within coals and sediments. To date, and to the author's knowledge, there are no published studies which have utilised these "modern" optical techniques of reflected-light and fluorescence microscopy to assess the amount, type and maturity of organic matter within the Carboniferous of the Midland Valley of Scotland.

Published chemical analyses of organic materials in the area relate mainly to the identification of compound classes within retorted oils, which were undertaken during the period when the oil-shale industry flourished. More detailed analyses were not possible until the development of more advanced analytical equipment such as the gas chromatograph, which is now often interfaced with a mass spectrometer and associated data-processing systems and permits the rapid identification of individual molecular components. The increased sophistication and sensitivity of this equipment, particularly over the last ten years, now enables valuable information to be gleaned about the type and maturity of components within the soluble organic fraction of coals and sediments.

The value of organic geochemistry and petrology as tools in petroleum exploration has been increasingly recognised over the past few years, and although studies of organic matter within the Midland Valley do exist, these are almost exclusively in the form of confidential oil and service company reports which have been produced during recent reappraisals of UK onshore hydrocarbon reserves. A few preliminary organic geochemical analyses have been published on a handful of samples, but these are restricted to the study of bitumens and to their potential source rocks. These investigations are clearly too sparse to provide a meaningful assessment of organic matter variation, source-rock potential and hydrocarbon occurrence within the Midland Valley as a whole, particularly in view of the overall abundance of organic matter of wide-ranging composition throughout the Carboniferous and its deposition in a variety of sedimentary environments. The pervasive nature of igneous activity within the Carboniferous of the Midland Valley is an added complication and although, as mentioned above, some hydrocarbon generation from oil shales in close contact with igneous masses has long been inferred, the extent to which intrusive and extrusive igneous activity affects organic matter has never been systematically evaluated. Neither has there been any study of the relative importance of maturation effected through the "normal" process of coalification *viz.* by the background geothermal gradient, as against maturation induced by rapid heating resulting from igneous activity.

It is the intention of this thesis to fill an obviously large gap in the literature relating to the study of organic matter within the Carboniferous succession of the Midland Valley of Scotland. The overall aim has been to conduct an organic petrological and geochemical evaluation of organic-matter type and maturity variation within the Carboniferous rocks of the eastern and cen tral Midland Valley. In addition to the petrological and geochemical characterisation of the various types of organic matter contributing to the sediments, several oils and bitumens have been investigated with consideration given to the mode of formation, timing of generation and potential source rocks. The maturation study has focussed on two main objectives. The first of these has been to establish the extent to which the background geothermal gradient has been modified through igneous activity; both laterally through the preparation of rank maps based on vitrinite reflectance data, and vertically, by constructing borehole-reflectance profiles. Estimates of the lateral variation in the background maturation level prior to major intrusive episodes have also been attempted. The second aspect of the maturity evaluation has been to assess the manner in which the optical and geochemical properties of organic matter of various types respond to differing heating rates within the geological environment.

The interpretation of all the results within a geological framework enables a reconstruction of the maturation history of the Midland Valley throughout the Carboniferous. It is hoped that the results will not only be of interest *per se*, but will assist in any future appraisals of hydrocarbon prospects within the Midland Valley.

CHAPTER 1

GEOLOGICAL BACKGROUND

1.1 INTRODUCTION

The structural and lithological complexity observed within the Midland Valley has resulted in the formulation of numerous and often conflicting models to account for the tectonic, structural and stratigraphic evolution of the province through geological time. A detailed analysis of the various models lies outside the scope of the current project, and so it is the intention of the following sections to present a brief, but balanced review of work which is widely considered to have contributed most to the elucidation of the geological history of the area and to outline interpretations which feature prominently in the most recent literature. In addition to the references cited, more thorough appraisals are contained in the publications of Craig (1983), Cameron and Stephenson (1985), Miller *et al.* (1987) and Besly and Kelling (1988).

1.2 TECTONIC FRAMEWORK

The Midland Valley of Scotland comprises a large fault-bounded trough or graben floored mainly by Devonian and Carboniferous sediments and volcanics. The structure is roughly 80km wide and extends onshore for approximetaly 200km from the Firths of Forth and Tay in the northeast to the Firth of Clyde in the south-west (Fig.1.1). The graben can be traced for a further 300km southwestwards into Ireland where it narrows to approximately 50km and becomes less clearly defined due to obscuring of the major bounding faults by post-Palaeozoic sedimentary cover.

The Midland Valley is first recognisable as a discrete structural unit after the Caledonian orogeny (Kennedy 1958; George 1960). Over the past twenty years, following the work of Dewey (1969, 1971), this major event has been interpreted within the context of plate tectonics and is widely accepted as being the result of plate interactions at a destructive plate margin. During this period, the Midland Valley graben was intitiated either as a fore-arc (Leeder 1982) or inter-arc (Bluck 1983) basin which developed in response to the northward subduction of a slab of oceanic crust. This plate underthrust the southern margin of the North American landmass throughout the early Palaeozoic, effecting the closure of the Iapetus Ocean and resulting in the subsequent emplacement of the Southern Uplands landmass which is widely considered to be the remains of an accretionary prism that accumulated at the leading edge of the subducting plate (McKerrow *et al.* 1977; Leggett *et al.* 1979). Final suturing of the North American and European landmass was achieved by the Mid-Devonian, at which time the Midland Valley had become increasingly important as a major intracratonic sedimentary basin.

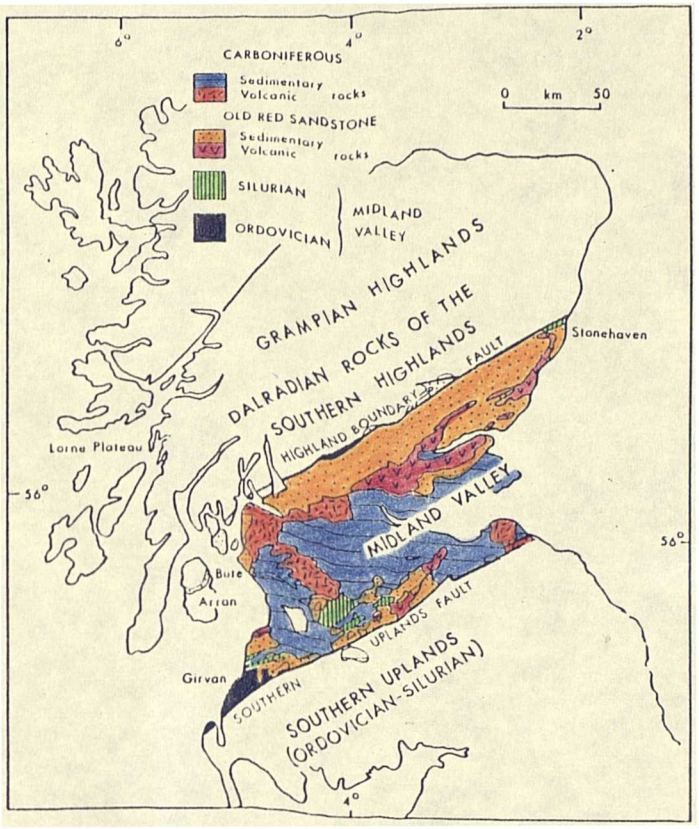


Fig.1.1 Sketch map of the Midland Valley of Scotland and adjacent regions (modified from Bluck 1984).

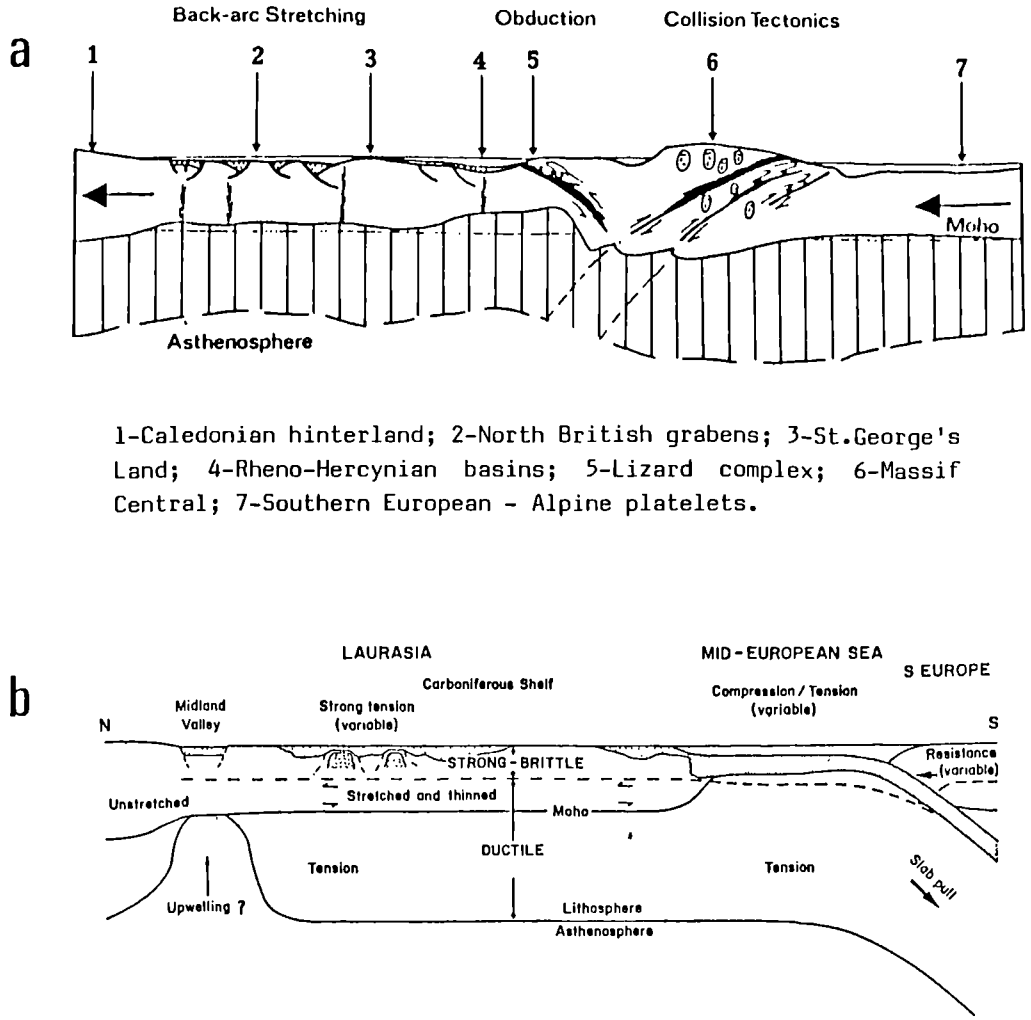
Throughout the Upper Palaeozoic, the Midland Valley lay on the northern margin of the developing Variscan orogenic belt which constituted a zone of active microplate collision resulting from the convergence of the Euramerican and Gondwana landmasses (Rast 1983). Although lying outside the main deformation zone, the subsequent geological evolution of the Midland Valley was strongly influenced by the tectonic processes active within the main orogen to the south. The most important controlling factor linked to the developing orogen is recognised to be lithospheric stretching, which was instrumental in initiating the subsidence of many Upper Palaeozoic basins within the British Isles (Dewey 1982; Leeder 1982). Evidence supporting the theory that active crustal extension occurred throughout the Upper Devonian and Lower Carboniferous of Britain derives from the delineation of fault-bounded basins, many of the characteristic half-graben type (Leeder 1976,1982), the occurrence of extensive intra-continental volcanism and the discovery of other indicators of high regional heat flow, for example, the presence of widespread stratiform base metal mineralisation in Ireland (Boyce *et al.*1983). As well as these regional studies, local sedimentological

analyses in the Northumberland and Pennine basins have identified facies and faunal distributions, particularly over tilt-block margins, which are all consistent with sediment accumulation within a Dinantian tensional stress system (Leeder 1987; Leeder and McMahon 1988). This extensional tectonic regime was responsible for the development of the well-defined E-W orientated "block and basin" topography characteristic of British Dinantian stratigraphy (Bott 1967). Under tensional stress, remnant Caledonian granitic intrusions persisted as structural highs (blocks) whilst the intervening areas, not underlain by buoyant granitic masses, formed grabens. Differential subsidence led to attenuated sedimentary sequences developing over the structural highs and thick successions accumulating in the basins.

In many northern and midlands Carboniferous provinces, differential subsidence either died out or became less pronounced in Namurian times, when regional downwarping dominated and resulted in blocks and basins subsiding together throughout the rest of the Carboniferous (Johnson 1982; Bott 1987). Unlike most other Carboniferous provinces, major volcanic activity in the Midland Valley was not confined to the Dinantian, and its persistence throughout the Carboniferous led to the concomitant maintenance of differential subsidence. The latter probably reflects continued crustal instability in the Midland Valley, related to its proximity to the Caledonian suture zone (Johnson 1982).

The extensional control on Upper Palaeozoic sedimentation and stratigraphy is now widely accepted, but there is still much speculation about the causative mechanism. Although most models identify Hercynian plate movements as the underlying driving force for lithospheric stretching, opinion is still fundamentally divided as to the precise method of basin initiation. Leeder (1982) advocates a back-arc rifting mechanism by means of extensional tectonics operating within the overriding plate on which he considers the British Isles to be located during the Upper Palaeozoic (Fig.1.2a).

Bott (1967) and Johnson (1981), however, have found no evidence for a northward-dipping subduction zone within Britain at this time, and they interpret the UK Carboniferous province to be attached to a southward-subducting crustal slab. Differential strain in the upper and lower crust, resulting from slab-pull, is invoked to explain basin formation and development within the Carboniferous (Bott *et al.* 1984; Bott 1987). To compensate for the differential strain between the brittle upper crust and the ductile lower crust, it is thought that some upwelling of the asthenosphere into the lithosphere may have occurred at the northern margin of the stretched region, i.e. below the Midland Valley (Fig.1.2b).



1-Caledonian hinterland; 2-North British grabens; 3-St.George's Land; 4-Rheno-Hercynian basins; 5-Lizard complex; 6-Massif Central; 7-Southern European - Alpine platelets.

Fig.1.2 Contrasting models for the origin of Carboniferous subsidence in Britain and Europe (Fig.1.2a modified from Leeder 1987; Fig.1.2b modified from Bott 1987).

Both the above models envisage crustal stretching within a N-S stress field.

A contrasting and more controversial hypothesis is presented by Haszeldine (1984, 1988) who views Carboniferous basin formation as occurring independently of the structural evolution of the Variscan orogenic zone. E-W tension associated with early rifting in the proto-North Atlantic is postulated to explain the presence of numerous lineaments or "geofractures" which transect the UK. The N-S orientation of many Midland Valley sedimentary basins in Namurian times has been cited in support of the Haszeldine model (Stedman 1988), but the theory founders badly on many geological points, discussed by Leeder (1988). The most important of these relates to the recent re-dating of the Carboniferous time-scale which now places any supposed Carboniferous rifting events firmly within the Permian or even later. Furthermore, it is difficult to accommodate the E-W and NE-SW fault structure in the Midland Valley within an E-W tensional system (Read 1988).

In an evaluation of much of the currently available structural and stratigraphic data, Read (1988) concludes that the factors governing Carboniferous sedimentation within the Midland Valley conform most closely with the model of Dewey (1982). He infers that right-lateral, strike-slip faulting superimposed on basin subsidence more suitably defines the present-day disposition of structural features in the Midland Valley, rather than pure shear resulting from the dominantly N-S or E-W tensional regimes invoked in other models.

Attempts to interpret Upper Palaeozoic basin evolution in Britain within a broader context have been undertaken by Dewey (1982) and Leeder (1982) who have applied the extensional theory of McKenzie (1978), which had already been successfully tested in many Mesozoic basins lying at passive continental margins and in back-arc environments (e.g. Sclater and Christie 1980). The model proposes that in areas of high heat-flow, fault-bounded basins are initiated in response to lithospheric extension. Following this phase of crustal thinning, the lithosphere cools and thickens back to its pre-extension thickness, promoting basin subsidence. The earlier "McKenzie" stretching event has been equated with the development of the "block and basin" topography in the Dinantian, with accompanying volcanism also indicating high heat-flow. This later gave way to a regional thermal sag phase, broadly corresponding with Namurian and Westphalian sedimentation, when the blocks and basins lost their separate identities. The McKenzie model fits reasonably well with the observed patterns of sedimentation in the Midland Valley, but some modification is needed to incorporate the persistent differential subsidence which, as mentioned previously, was linked to contemporaneous volcanic activity.

Detailed work in Carboniferous basins in northern England has indicated that crustal stretching had been around fifty per cent (Dewey 1982; Leeder and McMahon 1988). An accurate value has not yet been obtained for the Midland Valley as the presence of non-compacting volcanics in the succession has meant that the most recent tectonic subsidence calculations could not be applied to basins of this kind.

Objections to the application of the McKenzie model to Upper Palaeozoic basin subsidence are raised by Bott (1987) who maintains that there is insufficient geological evidence for crustal stretching having been as great as that required by the hyothesis. Furthermore, he calculates that the rate of Silesian subsidence in many Pennine basins has been far more rapid than would be expected for McKenzie-type thermal subsidence. In the light of this evidence, Carboniferous basin evolution is interpreted entirely within a lithospheric-stretching framework, which was not restricted to the Dinantian.

Basin subsidence is therefore attributed to a continuing tensional-stress system rather than to thermal sagging as proposed by McKenzie.

Clearly, much more work is required in Silesian basins to establish the exact degree of fit of the McKenzie model with Upper Palaeozoic basin development in Britain. It seems likely, however, that that Upper Palaeozoic history of the Midland Valley of Scotland corresponds at least in part to the evolution from youth to maturity of a large rifted basin. Thefinal subsidence or sag phase was terminated in Westphalian/Stephanian times by deformation and basin inversion which marked the final stages of continental collision in the Hercynian orogeny. Renewed tensional stresses led to the emplacement of a tholeiitic dyke suite and the associated Midland Valley Sill complex, long-considered to be of Stephanian age, but now assigned to the Permian on the basis of recent geochronological data (Lippolt *et al.* 1984).

Little is known of the post-Palaeozoic tectonic development of the Midland Valley since no strata or structures attributable to this part of the geological history have yet been discovered. It seems probable that throughout Mesozoic and later times the Midland Valley of Scotland was maintained as a structural high, in marked contrast to its preceding role as a major graben during the Palaeozoic eon.

1.3. STRUCTURE

1.3.1 Deep Structure

Although much attention has been directed towards the tectonic and structural evolution of the Midland Valley, there is still relatively little information about the nature and configuration of the basement. This stems from the limited occurrence and the paucity of exposed Lower Palaeozoic sediments and an absence of *in situ* older strata within the area.

Kennedy (1958) and George (1960) were the first workers to suggest that the Midland Valley has a pre-Caledonian basement, and this has been substantiated by the discovery of crustal xenoliths in Carboniferous and Permian vents (Upton *et al.* 1976, 1983) and also from the study of crystalline clasts in Ordovician and Silurian conglomerates (Longman *et al.* 1979).

Further advances towards an understanding of the deep structure of the Midland Valley were achieved following the interpretation of seismic profiles (Bamford *et al.* 1977; Bamford 1979). A diagrammatic summary is shown in Fig.1.3 which reveals that the superficial Midland Valley graben corresponds at depth with a horst-like mass. The high-grade basement is probably gneissic and occurs at depths of approximately 8-15km below the present-day land surface. Results from

more recent seismic (Conway *et al.*1987), gravity and aeromagnetic surveys (Hipkin and Hussain 1983; Davidson *et al.* 1984) concur with the general model presented in Fig.1.3.

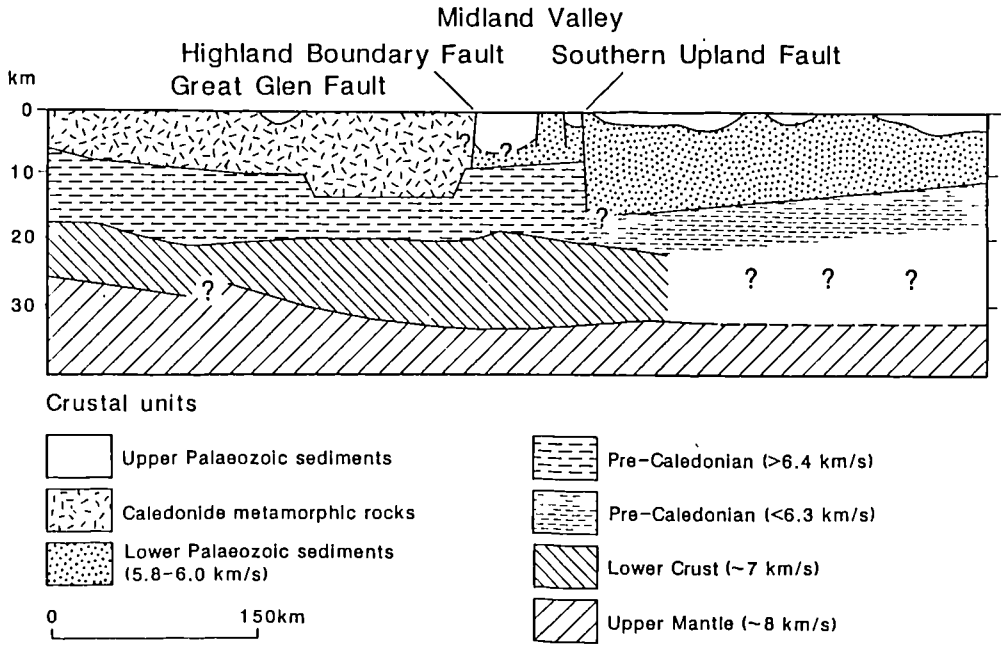


Fig.1.3 Deep structure of the Midland Valley of Scotland and adjacent regions (from Cameron and Stephenson 1985; modified after Bamford 1979).

1.3.2 Surficial Structure

The broad-scale structure of the Midland Valley is relatively simple, being a graben bounded by the NE-SW-trending Highland Boundary and Southern Uplands Faults which appear to be surface expressions of much deeper crustal lineaments (Fig.1.3). These fractures originated in the Caledonian Orogeny and their present location coincides roughly with the former margins of this major ensialic basin complex. The interaction of folding, faulting and volcanism has resulted in the formation of three major sedimentary basins which, from NE to SW, are the Fife-Midlothian, the Stirling-Clackmannan-Central Coalfield and the Ayrshire Basins. This apparent simplicity belies the true structural complexity of the region, the main features of which are shown in Fig.1.4.

Four major sets of structural features can be identified:-

(i) a series of approximately N-S-trending folds which have sigmoidal axes and curve towards the northeast in the north of the area and towards the south-west in the south. These axes are best developed in the northeastern Midland

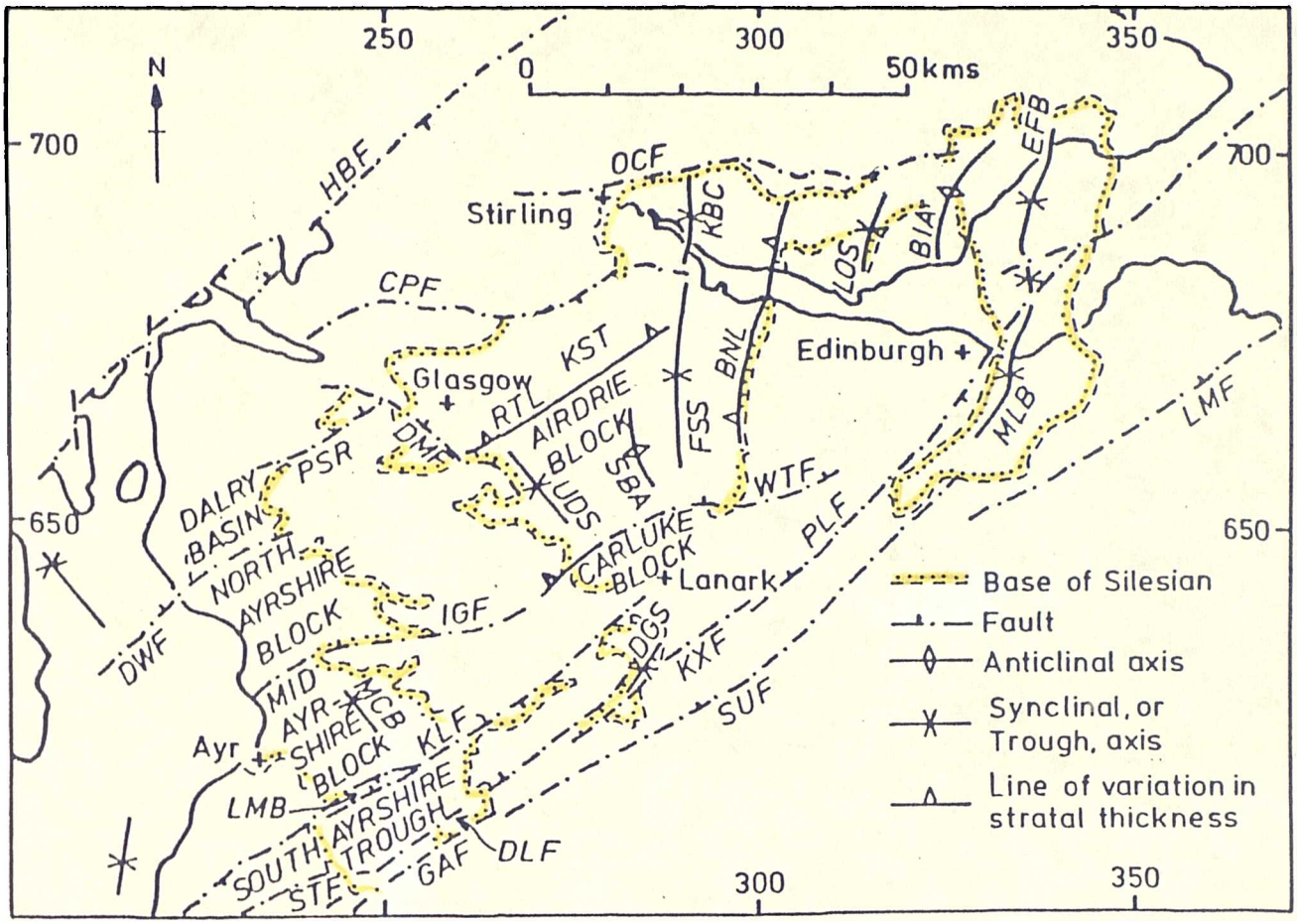


Fig.1.4 Major structural units controlling sedimentation in the Midland Valley (modified from Read 1988). Base of Silesian shows ornament on the deposit side. Faults have crossmark on the side of apparent downthrow. Lines of stratal thickness variation have triangular mark pointing in the direction in which the strata thicken. Abbreviations: *BIA*, Burntisland Anticline; *BNL*, Bo'ness Line; *CPF*, Campsie Fault; *DGS*, Douglas Syncline; *DLF*, Dalmellington Fault; *DMF*, Dechmont Fault; *DWF*, Dusk Water Fault; *EFB*, East Fife Basin; *FSS*, Falkirk–Stane Syncline; *GAF*, Glen App Fault; *HBF*, Highland Boundary Fault; *IGF*, Inchgotrick Fault; *KBC*, Kincardine Basin–Clackmannan Syncline; *KLF*, Kerse Loch Fault; *KST*, Kilsyth Trough; *KXF*, Kennox Fault; *LOS*, Lochore Syncline; *LMB*, Littlemill Basin; *LMF*, Lammermuir Fault; *MCB*, Mauchline Basin; *MLB*, Midlothian Basin; *OCF*, Ochil Fault; *PLF*, Pentland Fault; *PSR*, Paisley Ruck; *RTL*, Richey Line; *SBA*, Salsburgh Anticline; *STF*, Straiton Fault; *SUF*, Southern Uplands Fault; *UDS*, Uddingston Syncline; *WTF*, Wilsontown Fault.

Valley and are represented by structures such as the Lochore Syncline, the Burntisland Anticline and the Fife-Midlothian Basin. The present-day fold axes are slightly offset from the axes that existed at the time of sedimentation (Goodlet 1959; Stedman 1988), providing some support for the suggestion that strike-slip tectonics influenced the formation of at least some structures during the Carboniferous (see Section 1.2);

(ii) a set of NE-SW-trending structures (mainly faults), lying approximately parallel to the Highland Boundary and Southern Uplands Faults. These probably represent reactivated Caledonian basement fractures. Many of these faults had large throws, were active throughout the Carboniferous and exerted a significant control on sedimentation (Richey 1935). Examples

include the Dusk Water, Kerse Loch and Pentland Faults;

(iii) a series of ENE-WSW and E-W orientated structures of which the Ochil and Campsie Faults are the most important representatives. Although the Ochil Fault is known to have been active throughout the Carboniferous (Francis *et al.* 1970), other faults in this suite were formerly held to be entirely associated with the intrusion of the Midland Valley tholeiite complex during late Carboniferous (now Permian) times. More recent work has shown that at least some of these E-W fractures, e.g. the Abbey Craig and Alloa Faults, were also synsedimentary features (Francis and Walker 1987); and

(iv) a set of NW-SE and WNW-ESE structures, principally fault-bounded troughs, which are best developed in the Ayrshire Basin. Although some of these structures may have been active in the Viséan (Hall 1974), the majority are thought to post-date the E-W fault system and probably had a major influence on Permian sedimentation in the Mauchline Basin (Mykura 1967) and adjacent areas (Hall *et al.* 1984).

Most faults have experienced normal dip-slip movements, but some, such as the Highland Boundary and Pentland Faults, are high-angle reverse faults. Strike-slip movement is known or suspected on many faults in the Midland Valley, but the lack of field evidence invariably makes this difficult to prove (see Read 1988 for discussion). Many large faults are really conjugate or *en echelon* fault zones rather than individual fractures and have often experienced variable and complex histories of movement.

1.4. DEPOSITIONAL HISTORY

The interplay between structure, volcanism and sedimentation is perhaps the most characteristic feature of the Upper Palaeozoic depositional history of the Midland Valley and was particularly pronounced during the Carboniferous period.

In Devonian times, there was a general imbalance between tectonics and sedimentation which gave rise to the development of large fault-scarps and rift structures (Wilson 1980; Bluck 1983). In marked contrast, Carboniferous tectonics generally kept pace with sedimentation resulting in the accumulation of very thick successions which, if interrupted by faulting, volcanism or the presence of structural highs, promoted pronounced variations in sediment thickness.

Stratigraphic details relating to pre-Carboniferous sedimentation are not included in the following account since this thesis deals solely with the analysis of samples from Carboniferous sequences to which more weight is accordingly given.

1.4.1 Pre-Carboniferous Sedimentation

The oldest sediments preserved in the Midland Valley are of Ordovician age and are exposed, along with Silurian strata, in small inliers located mainly along the southern flanks of the area. The sediments consist largely of discrete wedges of shallow-water marine shales, sometimes accompanied by cherts and pillow lavas which grade into increasingly coarse turbiditic sequences. This distinct stratigraphic assemblage and the repetitive, northward-younging nature of the sequences are consistent with their development as imbricate thrust sheets which formed part of an accretionary prism at a destructive plate margin (McKerrow *et al.* 1977; Leggett *et al.* 1979). Subsequent emergence of the trench-slope break to form part of the proto-Southern Uplands (Cockburnland) in early Silurian times isolated the Midland Valley inliers from the main trench to the south.

Recent work has cast some doubt on the importance of the accretionary prism model and suggests that the Southern Uplands may be the product of a more complex geological situation for which a sequential back-arc and foreland basin thrust model has been proposed (Stone *et al.* 1987). Whatever the mechanism for the formation of the Southern Uplands, by late Silurian times the Midland Valley was finally established as an inland basin, and progressive isolation from the sea is reflected by Upper Silurian sequences becoming increasingly continental in character.

Apart from the successions in the Lesmahagow and Hagshaw Hills inliers, there is a marked angular discordance between Silurian sediments and the overlying Devonian strata which represents the final major phase of intense folding associated with the Caledonian orogeny (Mykura 1983).

Devonian sedimentation in the Midland Valley is represented by the Lower and Upper divisions of the Old Red Sandstone which, in this area, are almost entirely terrestrial in character (House *et al.* 1977). The Midland Valley at this time constituted a major intermontane basin in which great thicknesses of predominantly red conglomerates and sandstones accumulated in a prevailing arid to semi-arid climate. The rocks outcrop in two major tracts running parallel to the Highland Boundary and Southern Uplands Faults, with an intervening belt of volcanic uplands. The sediments have long been recognised as molasse deposits (Kennedy 1958) where the source areas were the Grampian Highlands to the north and the newly formed Southern Uplands Caledonian terrain to the south. The edges of the Devonian basin were probably not far from the present positions of the Southern Uplands and Highland Boundary Faults as the sediments have been shown to coarsen and thicken towards these fractures (Bluck 1978).

Lower Old Red Sandstone sediments are mainly coarse conglomerates, which were deposited in coalescing outwash fans bordering the boundary faults, and finer

red sandstones which occurred more distally in braided streams and floodplains which drained towards the southwest (Bluck 1978; Morton 1979). The enormous thickness of Lower Devonian sediments preserved in the Midland Valley, some 9km in the Strathmore Basin (Armstrong and Paterson 1970), attests to major subsidence having occurred adjacent to the Highland Boundary and Southern Uplands Faults.

Volcanism was widespread in Lower Devonian times and is marked by the occurrence of thick sequences of interdigitating lava sheets accompanied by pyroclastics, both of which are frequently intercalated with contemporaneous fluviatile sediments. Petrographic and elemental analyses of the volcanics are remarkably consistent and are characteristic of the calc-alkaline rock suite which is generated at active continental margins. A model to explain Lower Devonian volcanism therefore invokes magma generation associated with the descending oceanic slab underlying the closing Iapetus ocean (Thirlwall 1981, 1982). The cessation of volcanicity at the end of Lower Old Red Sandstone times is taken to indicate the end of subduction and that the final suturing of the North American-European landmasses had occurred, thus marking the last stage of the Caledonian orogeny, termed the Acadian (Francis 1978a). Subsequent uplift and erosion resulted in denudation of the land surface in the Midland Valley , and consequently no sediments of the Middle Old Red Sandstone facies are developed in the area.

The Upper Devonian was deposited with marked angular unconformity on the Lower Devonian strata and the successions are markedly thinner, finer grained and lack volcanics. The Upper Old Red Sandstone facies consists mainly of fine to medium-grained red or buff-coloured alluvial sandstones with some siltstones and mudstones. Conglomerates are less common than in the Lower Devonian and tend to have a smaller clast size. Palaeocurrent directions indicate a reversal of palaeoslope which now lay towards the northeast. The Upper Devonian displays a general fining-upwards pattern, and the rocks become sedimentologically more mature. Cornstone horizons also become conspicuous in the upper parts of the succession and are indicative of reduced rates of sedimentation and low rates of subsidence during which caliche soils could form. This evidence all points to the achievement of tectonic quiescence at the close of Upper Devonian times.

The overall pattern of Devonian sedimentation is interpreted as representing a major depositional cycle occurring in the waning stages of the Caledonian orogeny (Bluck 1978). The initial development of coarse, petrologically immature conglomerates and volcanics which later gave way

to the deposition of mature, finer-grained sandstones and caliche soils reflects a response to the establishment of an increasingly subdued tectonic regime throughout Devonian times. A more detailed account of Lower Palaeozoic and Devonian palaeogeography and stratigraphy may be found in Walton (1983a,b) and Mykura (1983), whilst a review of pre-Carboniferous tectonic events is given by Bluck (1984).

1.4.2 Carboniferous Sedimentation

Perhaps the most distinctive aspect of Carboniferous sedimentation is its rhythmic nature. The sediments are mainly sandstones and mudstones with thin beds of limestone and coal which are arranged in cyclical units or cyclothems up to 30m thick, but usually averaging about 10m. The thickness of the units varies from place to place, but the cyclothems reach their maximum development, both in terms of thickness and frequency, in areas of greatest subsidence (Read and Dean 1967). Complete cycles are rare.

Although the general cyclicity of Carboniferous sedimentation is a well-established fact, much controversy still surrounds the causal mechanism. Tectonic, eustatic and sedimentological controls have all been advanced to explain rhythmic sedimentation, but it is probable that all mechanisms were operative at different times throughout the Carboniferous, with much interaction (Leeder and Strudwick 1987; Leeder 1988).

The lithological and faunal characteristics of the sediments are all indicative of shallow-water deposition, so the occurrence of exceptionally thick sequences in some areas (approaching 4km in east Fife) suggests that subsidence was broadly keeping pace with sedimentation throughout the period. Marked lateral variation in sediment thickness in different areas is a further notable feature of Carboniferous sedimentation and can be related to the effects of volcanism, to the control exerted by an inherited Caledonian structural grain or to a combination of both these factors.

1.4.2.1 Structural Controls on Sedimentation

Structural control by faulting exerted the most pronounced and widespread influence on Carboniferous sedimentation, particularly during the Dinantian when the "block and basin" topography prevailed. The blocks and troughs were separated by narrow hinge lines across which marked differential subsidence occurred, leading to attenuated sedimentary sequences developing over the structural highs and very thick successions accumulating in the adjacent troughs. The bounding

faults were mainly aligned in a NE-SW direction, and although they were related to Caledonian lineaments, some of these fractures continued to be active throughout the Carboniferous. Repeated syn-sedimentary movements led to abrupt variations in sediment thickness across these faults (Richey 1935; Goodlet 1959). This phenomenon is most commonly observed in the south and west of the Midland Valley and is exemplified by structures such as the Kerse Loch, Inchgotrick, Dusk Water and Wilsontown Faults which probably extended close to the contemporaneous depositional surface (Richey 1935). Synchronous movements are also inferred to have occurred along the Highland Boundary, Southern Uplands and Pentland Faults.

In the eastern and central Midland Valley, the Campsie and Ochil Faults were major influences on sedimentation in the Central Coalfield and Fife-Stirling depositional basins respectively, but much of the 3000m (maximum) throw on the Ochil Fault is probably post-Carboniferous (Francis *et al.* 1970). Some strike-slip movement on the Ochil Fault in Fife is inferred to explain the initiation and subsidence of the Westfield Basin (Read 1988). Syn-sedimentary basin sagging was sufficiently rapid to enable an exceptionally thick development of coals (Francis 1961; Brand *et al.* 1980). In addition to these local crustal instabilities, isopach maps show a general thickening of strata towards the northeast in the Lower to Upper Limestone Groups (Goodlet 1957; Kennedy 1958; Browne *et al.* 1985), which has been taken to indicate a progressive tilt of the Midland Valley floor in this direction, about a NE-SW hinge line located in the vicinity of Arran (Kennedy 1958). During Westphalian times, the influence of deep-seated faults was greatly reduced, and graben-tilt appeared to reverse, since isopach data show that major late Carboniferous subsidence occurred within the south and west of the Midland Valley.

In the eastern and central Midland Valley, sedimentary thickening and attenuation are more closely associated with a sequence of roughly N-S-aligned troughs and axes of uplift than to faulting. As mentioned previously, these structures display sigmoidal traces and were probably hinged to unknown basement structures. The serially-arranged uplifted structures are synonymous with the terms "highs" and "arches" and represent volcanically active anticlinal ridges of minimum subsidence. They were probably initiated in the Dinantian and were highly effective as barriers to sedimentation and faunal migration (Goodlet 1957; Wilson 1967). Although the barriers began to fail towards the end of the Dinantian, they persisted as active positive features and continued to influence sedimentation well into the Namurian. Representatives of these structures include the Bathgate, Salsburgh and Cousland highs and the Burntisland Arch. Of these,

the Burntisland Arch , lying on the eastern margin of a much wider arch-complex exerted the greatest and most long-lasting effect on the pattern of sedimentation within the eastern Midland Valley. This structure extends westwards and is terminated by a newly-named monoclinal hinge termed the Bo'ness Line which lies on the eastern flank of the Kincardine Basin (Read 1988). In post-Namurian times, this antiformal flexure separated the Fife-Midlothian and Stirling-Clackmannan-Central Coalfield Basins in which sedimentation was dominantly controlled by rapid basin subsidence. Some fault (or at least hinge) control is inferred in the Central Coalfield by the apparent link between the NE-SW trending Richey Line and the Dusk Water Fault of Ayrshire (Richey 1935; Read 1988; see also Fig.1.4).

Statistical analyses have shown that the arches were instrumental in determining the direction of sediment influx into adjacent basins (Read and Dean 1982).

1.4.2.2 Volcanic Controls on Sedimentation

Volcanic activity occurred sporadically, but persistently, throughout the Carboniferous and assumed a major role in governing the accumulation and disposition of sediments at this time. The most spectacular effect of volcanic control on sedimentation is exemplified by the Clyde Plateau Volcanic Formation in Dinantian times. This lava pile, up to 900m thick, formed an emergent landmass which separated the Ayrshire Basin in the west from the Lothians Oil-Shale Basin in the east (Greensmith 1968). Further volcanic activity in the Edinburgh district, represented by the Arthur's Seat Volcanics, helped to define further the margins of this restricted basin in which reduced sediment influx and the lack of turbulence promoted the accumulation and preservation of organic-rich shales.

Not only were the lavas of the Clyde Plateau Volcanic Formation important in forming a major dividing isthmus between two major sedimentary basins, their eruption on to what was already a differentially subsiding floor led to the inception of many other isolated or restricted basins which exerted a significant control on both contemporaneous and future patterns of sedimentation. Later variations in facies-type and sediment thickness are particularly marked in the Lower Limestone Group (Goodlet 1957) and can be related to differential basin subsidence within this undulating volcanic basement terrain. In some provinces, e.g. the Bathgate Hills, pronounced thickness variations in sediments overlying lavas have been shown to reflect the uneven contemporaneous erosion of lava surfaces (Jameson 1980, 1987).

Even after burial, volcanics continued to influence sedimentation by virtue of differential compaction. The thinning or absence of coals and argillaceous

sediments over bodies of incompactable volcanic rocks is often noticed and is accentuated by the presence of thick annular sandstone bodies (less compactable than shales) around the volcanic pile, where they originated from shoals of sand (Francis 1961b). Reduced thicknesses of strata attributable to differential compaction are also detectable over thick lava piles such as those occurring within the Rashiehill Borehole (Anderson 1963).

A structural control of volcanism is inferred from the alignment of many vents along fractures such as the Campsie (Craig and Hall 1975) and Ardross Faults (Francis and Hopgood 1970) and the location of lavas and pyroclastics on the crests or flanks of the structural highs referred to in the previous section. These factors strongly corroborate the notion that the anticlinal hinges and faults were linked to basement lines of weakness which provided conduits for ascending magmatic material (MacGregor 1948; Goodlet 1959; Francis 1967).

1.4.2.3 Stratigraphy

To gain a fuller appreciation of the nature and diversity of environments available for the accumulation of organic matter and their spatial and temporal relationships, brief descriptions of the lithologies and depositional environments occurring within each stratigraphic division are presented in the following sections. The account concentrates on sedimentation within the eastern and central Midland Valley since the project encompasses samples from these areas only. Any refinements of the depositional models derived from the organic geochemical and petrological analyses undertaken in the course of this work are discussed more fully in Chapter 4.

The most recent palaeogeographic and palaeoenvironmental interpretations are given by Browne *et al.* (1985, 1987) and Read (1988), based on syntheses of virtually all the currently available stratigraphic and structural data.

First, some consideration is given to the problem of correlation within the Carboniferous succession.

1.4.2.3.1 Correlation

The classification and correlation of Carboniferous rocks in the Midland Valley is based largely on lithostratigraphy (MacGregor 1960), since the sequence as a whole contains very few zonally diagnostic fossils. The lithostratigraphic system has proved to be effective in areas where coal and oil-shale mining have resulted in tight well control. It becomes more subjective in sequences such as the Calciferous Sandstone Measures of east Fife where marked lateral variations in facies and thickness, coupled with an incomplete knowledge of the structure of the

area mean that uncertainties still arise in the stratigraphic assignment of some sequences, e.g. the Randerston section (Forsyth and Chisholm 1977, p.31). Further difficulties emerge in trying to correlate Midland Valley stratigraphy with Carboniferous sequences in the rest of Great Britain and Europe. This stems from the paucity of goniatites in Scottish sequences (Currie 1954), which form the basis of Carboniferous correlation outside of the Midland Valley.

The greatest success in correlating Midland Valley sequences with those elsewhere has been achieved through the use of spores (Smith and Butterworth 1967; Neves *et al.* 1972, 1973) and non-marine bivalves (Calver 1969). The non-marine bivalves find their greatest application in the correlation of Coal Measures strata where the profusion and diversity of species during this time mean that, in contrast with preceding groups, virtually the whole of the Scottish Westphalian can be correlated with Coal Measures sequences in the remainder of Great Britain and the rest of Europe. The spores and non-marine bivalves have been used to establish a chronostratigraphy within which the Scottish lithostratigraphic divisions have been integrated (George *et al.* 1976; Ramsbottom *et al.* 1978).

More recent appraisals of Upper Palaeozoic stratigraphy have led to a formal re-classification of Lower Carboniferous and Upper Devonian strata which is shown in Figs 1.5a and 1.5b. Although the long-established "Calciferous Sandstone Measures" and "Upper" and "Lower Oil-Shale Groups" are now assigned to the Strathclyde and Inverclyde groups, the latter terms are still relatively new and not yet widely entrenched in the literature. Since virtually all of the existing stratigraphic information given in the Midland Valley literature cited in this thesis is based on the earlier classification, the retention of the old-established terms is felt to be entirely justified within the confines of the current work.

1.4.2.3.2 Calciferous Sandstone Measures (Strathclyde Group and, in part, Inverclyde Group)

This lithostratigraphic unit constitutes the lower and thicker division of the Dinantian in the Midland Valley.

The base of the Dinantian cannot be accurately defined in Scotland owing to the lack of zonally specific fossil species. Upper Devonian sediments pass conformably, but transitionally, into Lower Carboniferous strata with the base of the Dinantian being arbitrarily placed at the top of the highest cornstone-bearing unit known to be of Upper Devonian age. Interdigitation of cornstones with strata of undoubted Carboniferous age, coupled with the apparent equivalence of Upper Devonian and Lower Carboniferous facies in some areas, clearly renders the traditional lithostratigraphically convenient assignment unsatisfactory. Recognition of this problem has recently led to the grouping of cornstones and Lower

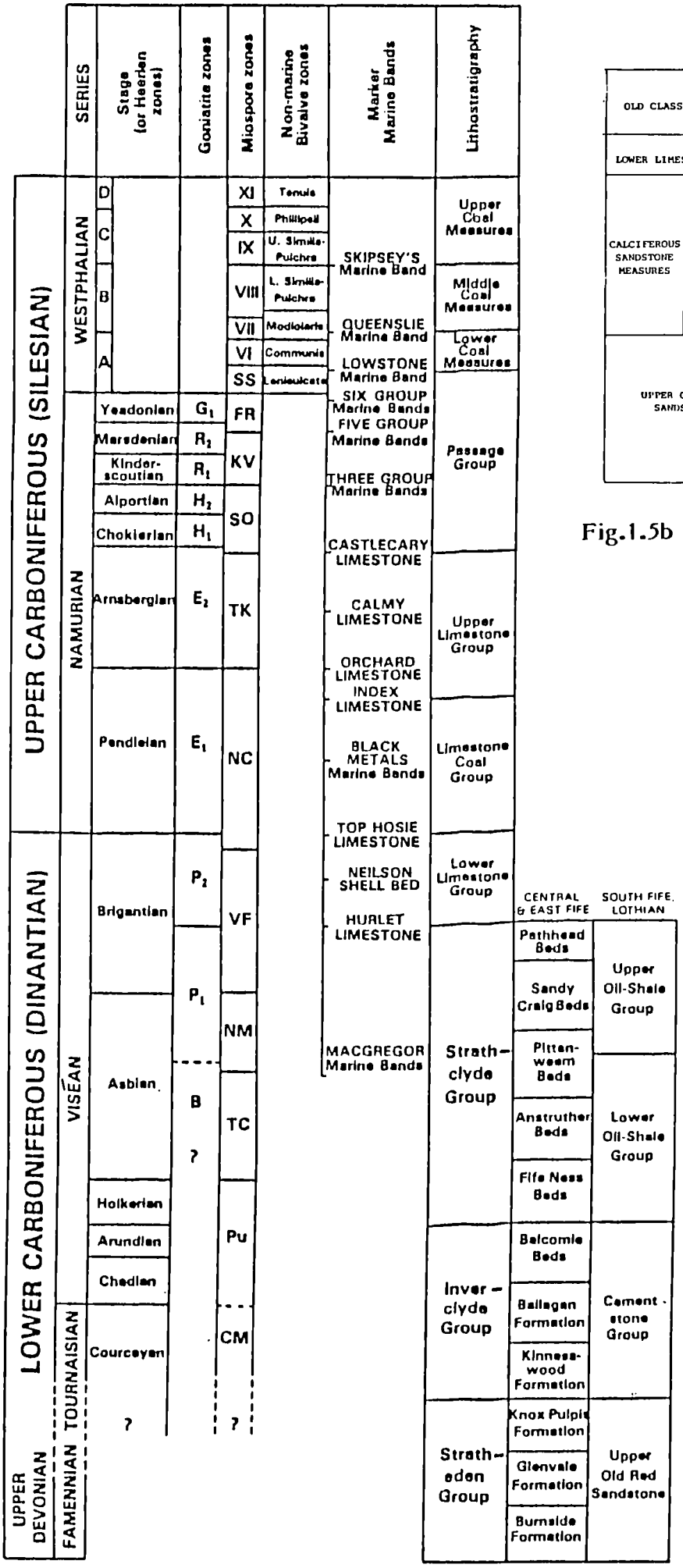


Fig.1.5a Upper Devonian and Carboniferous stratigraphy (modified from Browne *et al.* 1987).

OLD CLASSIFICATION		NEW GROUP CLASSIFICATION (Paterson and Hall 1986)	FORMATIONS
LOWER LIMESTONE GROUP		LOWER LIMESTONE GROUP	
CALCIFEROUS SANDSTONE MEASURES	UPPER OIL-SHALE GROUP	STRATHCLYDE GROUP (Lothian Oil-Shale Group)	Pathhead Sandy Craig
	LOWER OIL-SHALE GROUP		Pittenweem Anstruther Fife Ness
	CEMENTSTONE GROUP	INVERCLYDE GROUP	Balcomie Ballagan Kinnesswood
UPPER OLD RED SANDSTONE		STRATHEDEN GROUP	Knox Pulpit Dura Den Glenvale Burnside

Fig.1.5b Old and new classifications of Devonian and Carboniferous rocks in the Midland Valley (modified from Browne 1986).

Carboniferous strata of the same facies into one major lithostratigraphic division termed the Inverclyde Group (Paterson and Hall 1986).

The greatest thickness of Calciferous Sandstone Measures strata is found in West Lothian and Midlothian where the succession is approximately 3km. In this region the sequence consists of a basal cementstone facies and an upper oil-shale facies. The Cementstone Group is locally over 1km thick and comprises a series of interbedded thin cementstones (impure, fine-grained dolomitic limestones), mudstones and sandstones. The sequence is interpreted as having been deposited in lagoonal, coastal-flat environments where the presence of gypsum partings, salt pseudomorphs and desiccation breccias attest to the periodic development of highly saline waters and subaerial exposure in an arid climate (Greensmith 1965, 1968). Laterally equivalent facies in the central and western Midland Valley and west Fife are thought to be the Ballagan Formation and Balcomie Formation (Browne 1980). The former has not yet been found in east Fife.

In the middle/later part of Cementstone Group times, volcanic activity at the western end of the Midland Valley resulted in the accumulation of the thick subaerial lava pile of the Clyde Plateau Volcanic Formation. As mentioned previously, this formed a major barrier to sedimentation in the Dinantian by dividing the Midland Valley into two adjacent depocentres termed the Ayrshire Basin, to the west, and the Edinburgh Basin which lay to the east (Greensmith 1968).

In the Edinburgh Basin further intrabasinal volcanic activity, coupled with the gradual encroachment of a major delta system lying to the northeast, served to create a restricted depositional environment, termed Lake Cadell, in which shallow-water sediments of the Lothians Oil-Shale Group accumulated in a predominantly fluvio-deltaic regime. In this basin, the monotonous sabka-type cementstone facies was succeeded by over 2km of sandstones, mudstones, marls, thin coals and mainly non-marine limestones which display a marked rhythmic pattern of sedimentation. The freshwater Burdiehouse Limestone divides the sequence into the Upper and Lower Oil-Shale groups where the latter is more arenaceous in character than the former. The occasional presence of marine bands within the succession reflects periodic connections of the depositional basin with the sea which lay to the east. A palaeogeographic reconstruction of the Midland Valley in Oil-Shale Group times is shown in Fig.1.6.

The sedimentological characteristics of the succession all point to deposition within a slowly subsiding inland basin in which conditions of extreme tectonic quiescence occasionally prevailed and gave rise to the accumulation and preservation of large quantities of algal material which formed the bulk of the precursor organic matter of the Lothians oil shales (MacGregor 1938). These

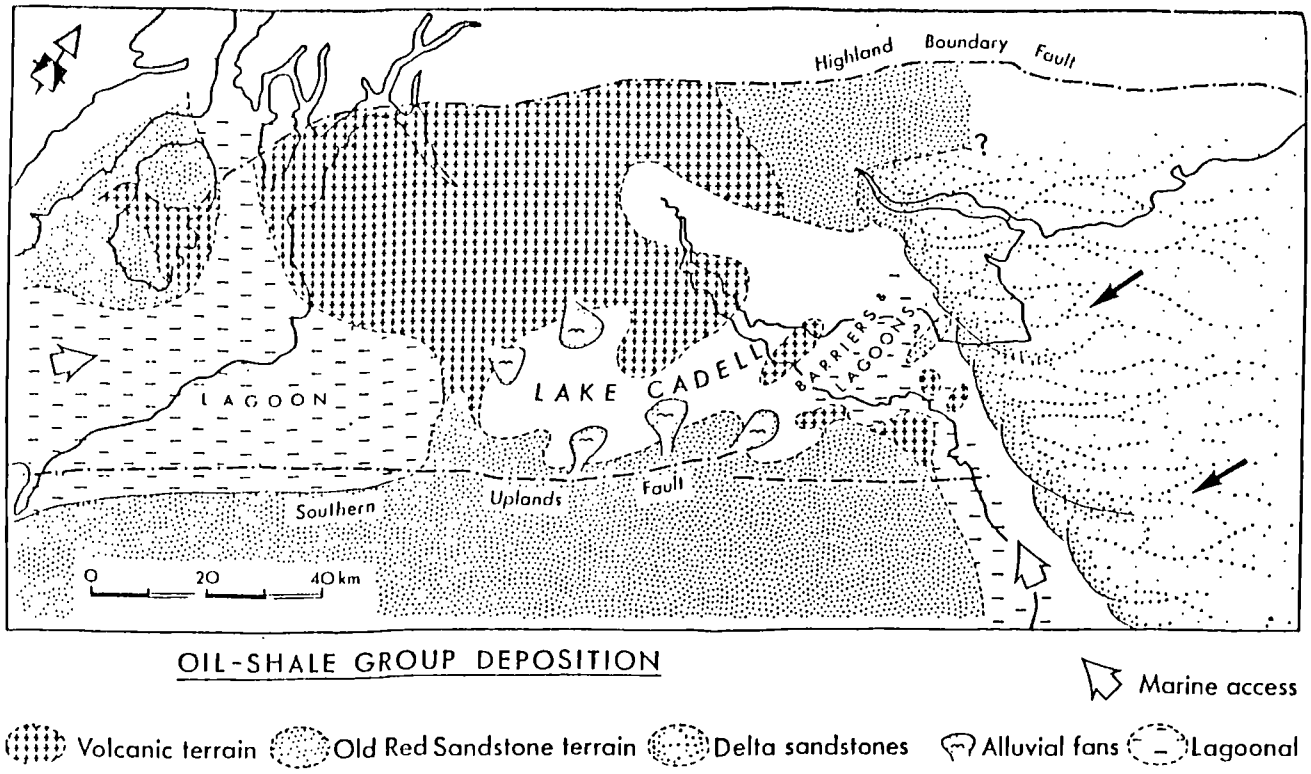


Fig.1.6 Oil-Shale Group depositional environments (from Loftus and Greensmith 1988).

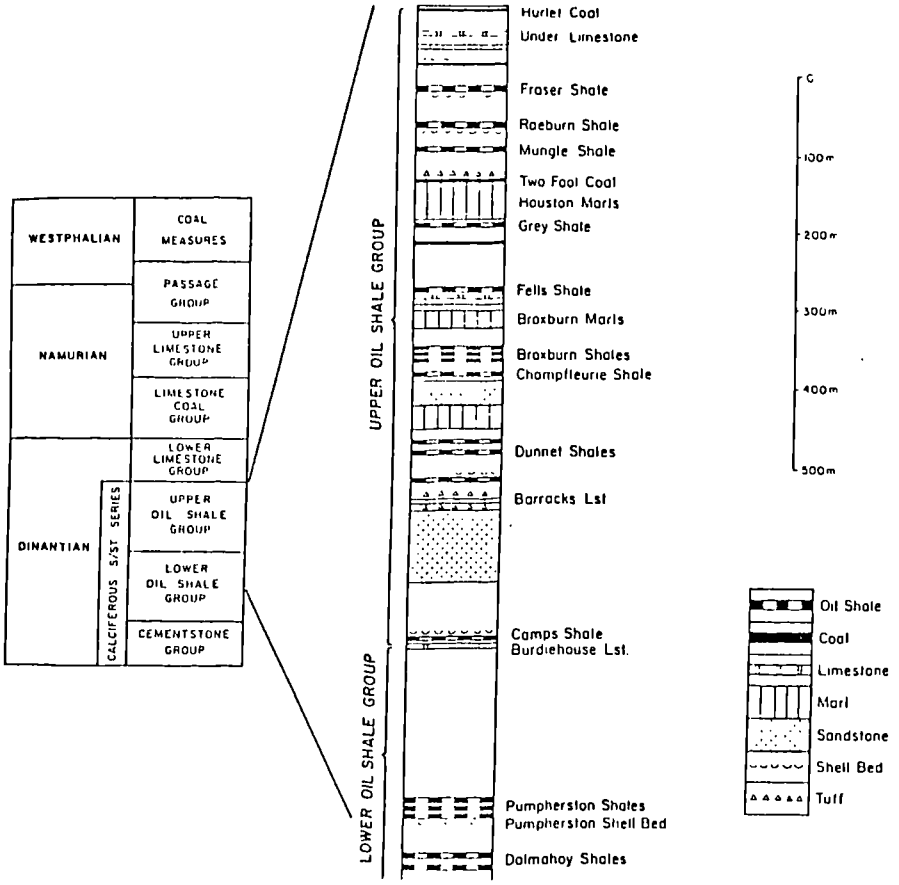


Fig.1.7 Generalised vertical section of the Lower Carboniferous sequence of the Lothians (from Parnell 1988, after Cameron and McAdam 1978).

deposits comprise approximately 3% of the total thickness of the Lothians succession (Greensmith 1962), and most of the 9-10 economically viable seams (some up to 5m thick) lie within the Upper Oil-Shale Group (Fig.1.7).

The rhythmic nature of Oil-Shale Group sedimentation is recognised as being a reflection of marked fluctuations in the water level of Lake Cadell brought about by the repeated advance and retreat of delta complexes within the depositional basin (Greensmith 1965, 1968; Loftus and Greensmith 1988). The underlying mechanism triggering the progradation and abandonment of the deltas is still a contentious issue (Leeder and Strudwick 1987). Opinion is also divided as to whether the petrographic features of the oil shales indicate that the organic matter accumulated within a perennial (Moore 1968; Loftus and Greensmith 1988) or playa-lake (Parnell 1988) lacustrine environment. The detailed organic petrological and geochemical evaluation of many oil-shales undertaken in this thesis has shed more light on this problem which is considered in Chapter 4.

Although confined principally to the south side of the Firth of Forth, the Lothians oil-shale field also extends northwards on to the south coast of Fife where the Dunnet Shale is the only recognised named seam (Carruthers *et al.* 1927). Apart from this marginal development of the Lothians oil-shale facies, the tripartite division of the Calciferous Sandstone Measures (CSM) is not recognised in Fife, where facies equivalents are mainly arenaceous, consisting of cyclical alternations of sandstones, limestones and shales (some carbonaceous) interbedded with thin coals and dolomites. Six lithostratigraphic divisions have been identified on the basis of coastal exposures. These are represented by the Balcomie, Fife Ness, Anstruther, Pittenweem, Sandy Craig and Pathhead Beds (see Fig.1.5a). Marked thickness and facies variations (a characteristic feature of CSM sedimentation), coupled with the paucity of inland exposures and a poorly elucidated structural history, mean that CSM sediments in Fife are mapped as a single lithostratigraphic unit.

The sequence totals over 2km in east Fife where most of the succession is exposed in coastal sections between Pathhead and Anstruther (Forsyth and Chisholm 1977). Thinner CSM sequences also occur in a northeasterly tract extending from the Cleish and Lomond Hills to East Neuk (Browne 1980). Correlations of these strata in different parts of the Midland Valley are shown in Fig.1.8.

The nature and distribution of CSM sediments in Fife are indicative of deposition within a large alluvio-deltaic complex which occupied the eastern part of the Midland Valley at this time (Courceyan-Brigantian) and helped to block the entry of the sea into Lake Cadell (Greensmith 1965, 1966). The presence of

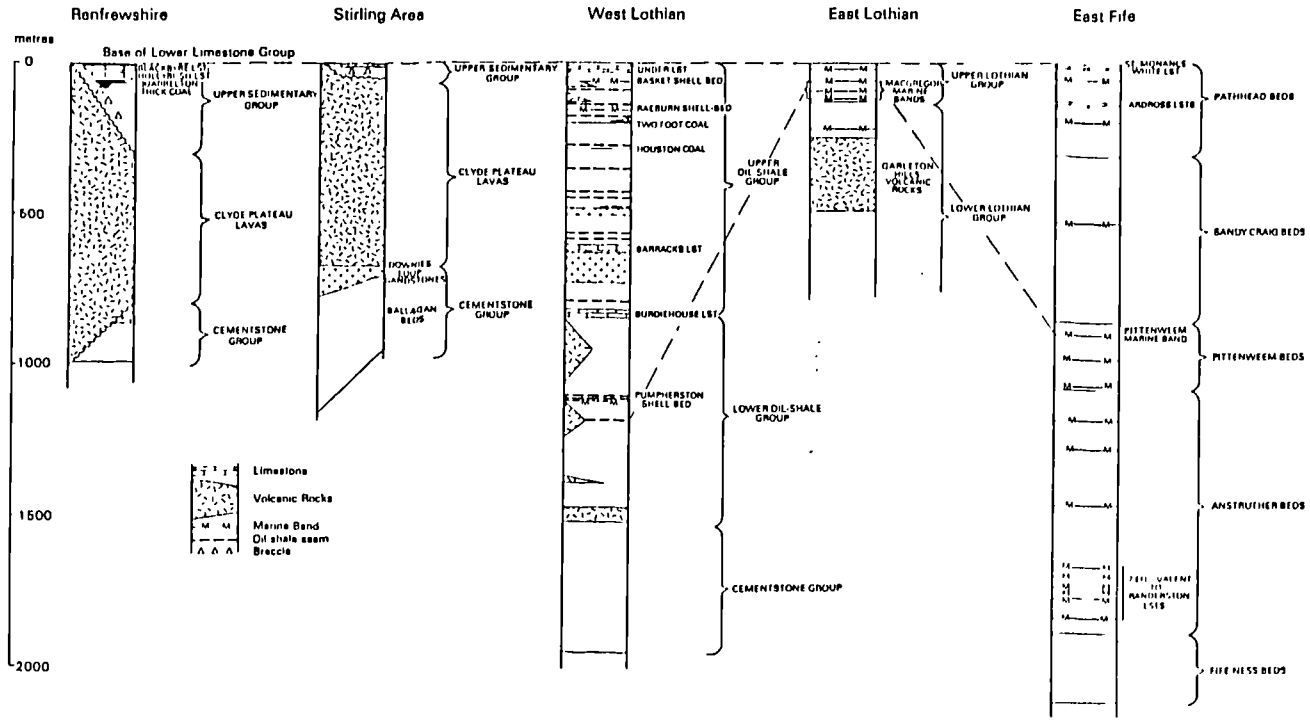


Fig.1.8 Comparative vertical sections of the Calciferous Sandstone Measures (from Cameron and Stephenson 1985)

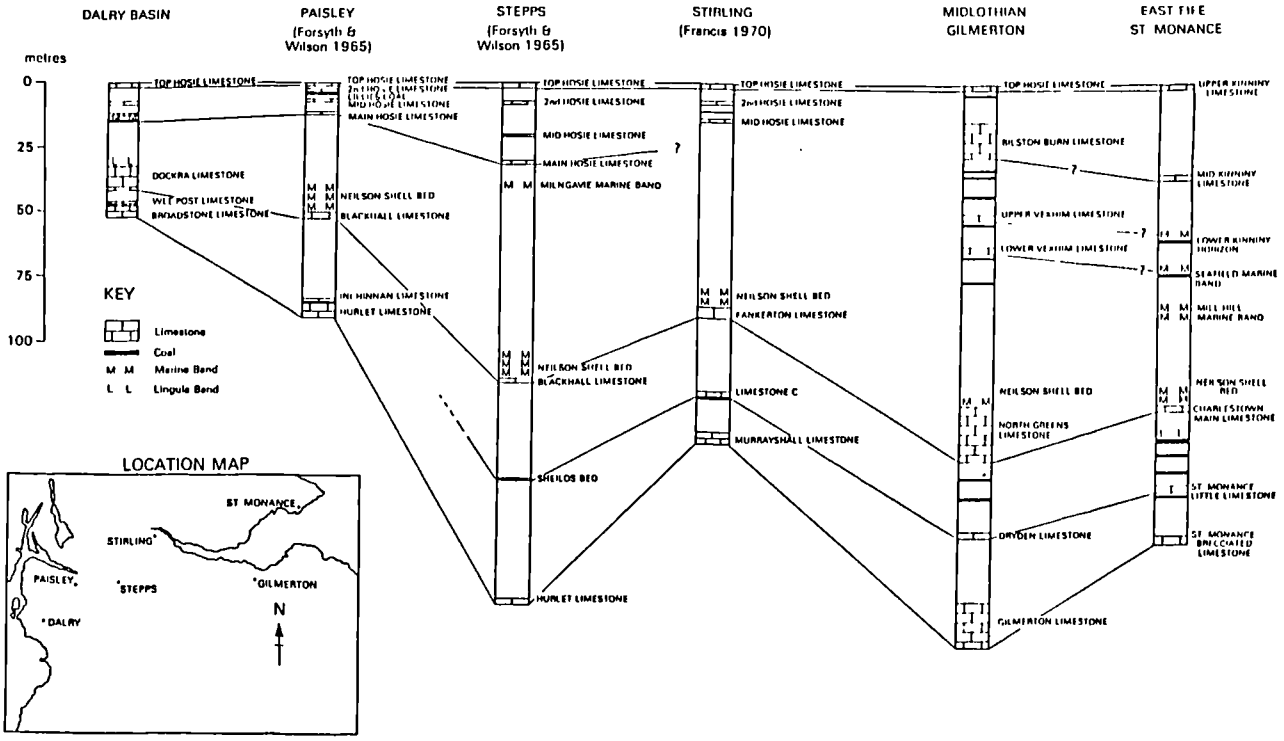


Fig.1.9 Comparative vertical sections of the Lower Limestone Group (modified from Cameron and Stephenson 1985).

marine limestones and shales within the Fife succession attests to the periodic inundation of the delta by the sea which lay to the northeast.

The overall picture of sedimentation in Calciferous Sandstone Measures times is therefore one of deposition on the western margins of a major Carboniferous delta system where there was a general balance between actively prograding delta fronts and the more tranquil lacustrine sedimentation within the Lothians Oil-Shale Basin.

1.4.2.3.3 Lower Limestone Group

This group constitutes the uppermost division of the Dinantian in Scotland and is generally conformable with the preceding Calciferous Sandstone Measures. The Lower Limestone Group includes the strata between the base of the Hurlet and top of the Top Hosie limestones in the central and western Midland Valley and their correlatives elsewhere (Fig.1.9). These limestones mark the first widespread marine transgressions in the Midland Valley and the incipient breakdown of many of the structural and volcanic barriers which influenced earlier Dinantian sedimentation. The Clyde Plateau Lavas and the Bathgate-Burntisland high persisted as broad areas of minimum subsidence throughout the period and separated three major depocentres constituting the Ayrshire, Central Coalfield and Fife-Midlothian Basins, which continued to be important sedimentary basins throughout the rest of the Carboniferous.

Strata in the Lower Limestone Group contrast with those of the Calciferous Sandstone Measures by being predominantly marine in character. They comprise rhythmic Yoredale-type sequences of marine shales and limestones with mainly fine- to medium-grained sandstones and occasional irregularly-developed coals.

Maximum sedimentation was attained in the Central and Fife-Midlothian Basins, with the thickest non-volcanic succession occurring in central and east Fife where over 220m of strata are represented (Forsyth and Chisholm 1977; Browne *et al.* 1986). Pronounced variation in sediment thickness is a conspicuous feature of Lower Limestone Group sedimentation which, as discussed in Section 1.4.2.1, has been attributed to fault-controlled differential subsidence in basins whose locations have been determined by the presence of underlying volcanics. Differential subsidence has also exerted a marked control on facies distributions, with greater proportions of sandstones occurring in thick, basinal areas whilst limestones and shales constitute greater parts of the succession in shelf areas overlying structural highs (Goodlet 1957).

The broad pattern of Lower Limestone Group sedimentation is consistent with deposition on a shallow-water marine shelf with relatively minor fluvio-deltaic influences. The generally thin coals in the sequence provide evidence for the reduction of water levels for only very short periods, enabling plant colonisation of the exposed land surface.

1.4.2.3.4 Limestone Coal Group

The Limestone Coal Group represents the lowest of the three divisions of Namurian strata in Scotland. The base of the succession is drawn at the top of the Top Hosie Limestone (Upper Kinniny of Fife), whilst the top of the group is placed at the base of the Index Limestone (not found in east Fife). The intervening strata are mainly terrigenous and are composed of a series of cycles of sandstones, siltstones, mudstones, seatearths and coals. The sequence is renowned for its numerous coals, many over 1m thick, and reaches its maximum development of 550m in the Kincardine Basin, within the northern part of the Central Coalfield Basin. The pattern of thickness and facies variation generally follows that of the Lower Limestone Group, with major controls on sedimentation resulting from differential subsidence and contemporaneous movements on NE-trending faults (Richey 1935; Francis *et al.* 1970). Abrupt lateral changes in sediment thickness accompanied by seam-splitting hinders correlation not only between basins, but between equivalent successions at different localities in the confines of the same basin. This problem means that laterally equivalent seams invariably possess different names (Fig.1.10).

The Limestone Coal Group is predominantly of fluvio-deltaic, non-marine character, but two major incursions are recorded by the Johnstone Shell Bed and Black Metals marine bands which occur in the lower and middle parts of the succession respectively. Numerous *Lingula* bands also attest to the periodic development of quasi-marine conditions (Forsyth 1980).

1.4.2.3.5 Upper Limestone Group

The lower and upper limits of the Upper Limestone Group are the base of the Index Limestone and the top of the Castlecary Limestone respectively. Structural controls on sedimentation initiated in the Dinantian continued to influence sedimentation, but regional subsidence began to become more important. Although cyclothemic sedimentation still persisted, there was a general reversion to major marine influences as in the Lower Limestone Group, which is indicated by the presence of many shales bearing rich marine faunas and also by the development of at least nine marine limestones. The thickest and most widely

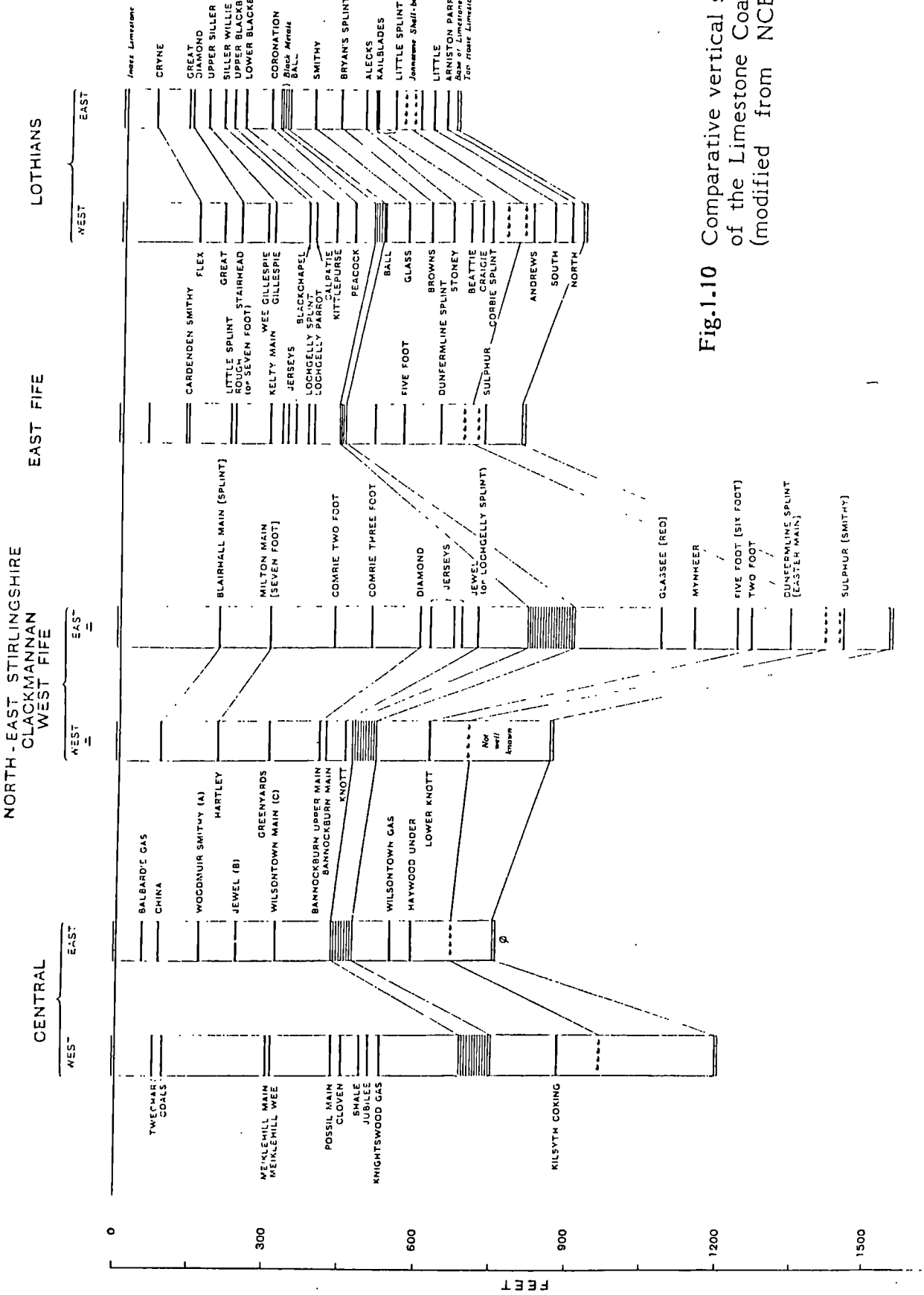


Fig.1.10 Comparative vertical sections of the Limestone Coal Group (modified from NCB 1960).

occurring of these limestones are the Index, Orchard, Calmy and Castlecary which form important correlative markers (Fig.1.11). Despite the many marine horizons within the group, the main lithological types are deltaic sandstones which often display erosive bases that cut out underlying strata in some areas. Many thin coals are also present.

The Kincardine Basin continued to be a major depocentre during Upper Limestone Group times with maximum subsidence occurring in the Gartarry area, represented by 590m of strata in the Gartarry Toll borehole (Francis 1956; Francis *et al.* 1970).

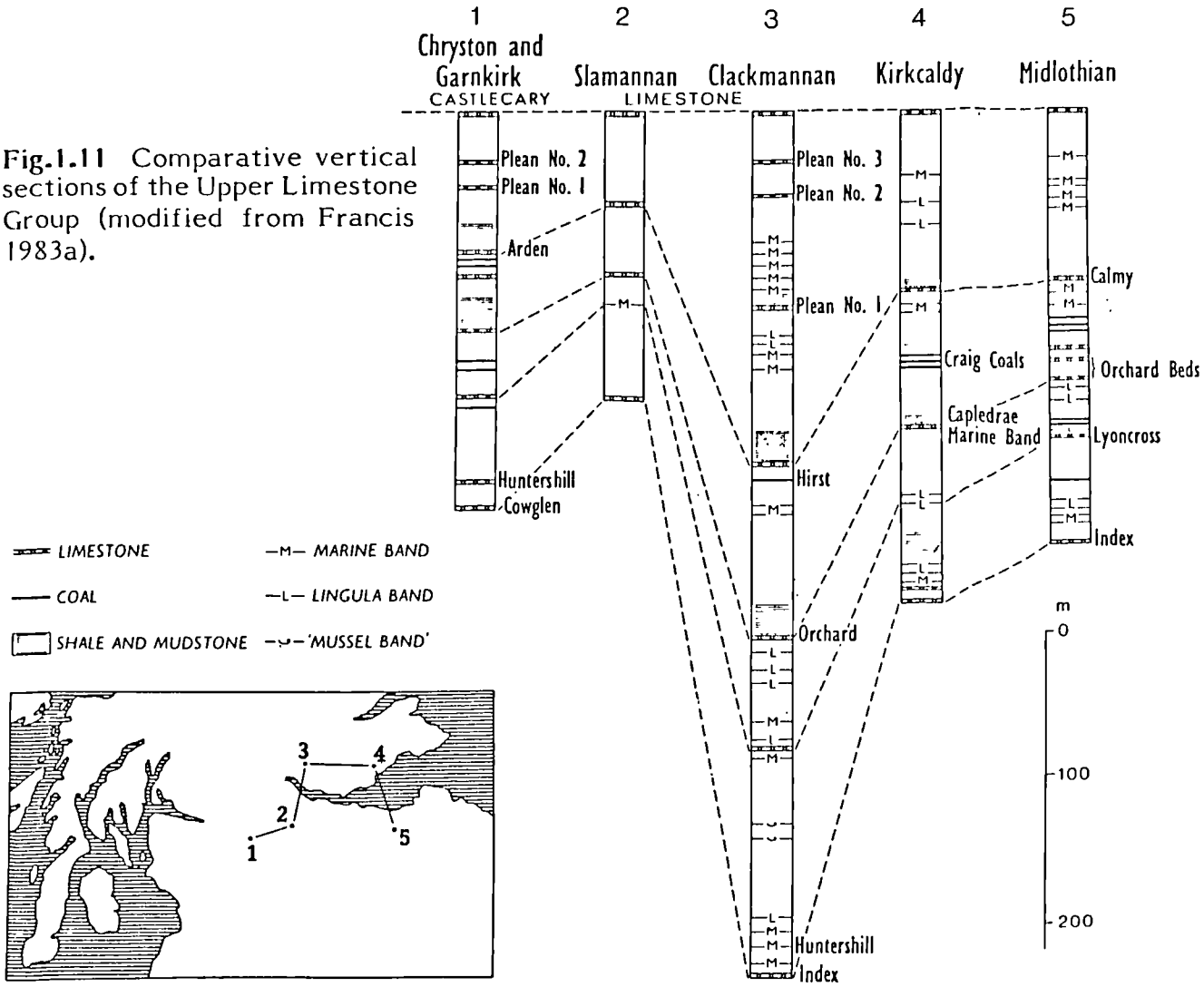


Fig.1.11 Comparative vertical sections of the Upper Limestone Group (modified from Francis 1983a).

1.4.2.3.6 Passage Group

Formerly known as the Scottish Millstone Grit (MacGregor 1960), the Passage Group constitutes the uppermost division of the Namurian in the Midland Valley and comprises strata between the top of the Castlecary Limestone and the local

base of the Coal Measures. Where the former is missing due to penecontemporaneous erosion, the base of the group is taken at a local unconformity above the highest recognisable Upper Limestone Group strata. The top of the sequence is drawn at the locally defined base of the Coal Measures in the various coalfields due to the absence of the definite goniatite zone (Section 1.4.2.3.1).

In contrast to the groups above and below, the Passage Group is dominantly arenaceous, reaching its maximum development of 380m in the Stirling-Clackmannan Basin (Browne *et al.* 1985). Rhythmic sedimentation is still operative,but is partially obscured by a predominance of thick alluvial sandstones (many with erosive bases) and the common occurrence of breaks in the sequence due to penecontemporaneous channel erosion. The presence of numerous thin marine horizons (mainly shales)in the thick, arenaceous sequence is indicative of rapidly alternating uplift and subsidence. This factor, in conjunction with the pervasive disconformities and rapid facies and thickness changes reflects the onset of a period of marked tectonic instability in Passage Group times which has been related to continental collision in the Massif Central (See Read 1988 for a discussion).

Many coal seams are present in the succession, but they are generally very thin, with the exception of those in the Westfield Basin,in which there is a unique development of Passage Group strata. This basin extends over only 3km^2 and forms a synclinal outlier on an antiformal high which separates the Central and Fife-Midlothian Basins. The basin is considered to have developed in response to movements on the Ochil Fault, which initiated structural inversion leading to the superimposition of this subsiding basin on a former volcanic high (Read 1988).

Although the Passage Group in the Westfield Basin is relatively thin (Fig.1.12a), the sequence is aberrant in that it is mainly argillaceous and contains an exceptionally thick development of coals. The major coal-bearing part of the sequence lies within the middle part of the Passage Group and constitutes a subdivision known as the Boglochty Beds (Brand *et al.* 1980).

A further conspicuous feature of the strata in the Westfield Basin is their abnormally rapid variation in thickness and lithology as they are traced over minor northeasterly fold axes (Fig.1.12b). Extreme thinning also occurs towards the basin margins. To accommodate this basinal sequence in so small an area requires not only that sedimentation keeps pace with basin subsidence, but that folding within the basin is contemporaneous with sedimentation. The Westfield Basin is therefore interpreted as a syn-sedimentary structure (Armstrong and Ewing 1971).

Within the Boglochty Beds lie two major oil-shale horizons known as the Westfield Oil Shale and the Westfield Canneloid Shale, both of which have been

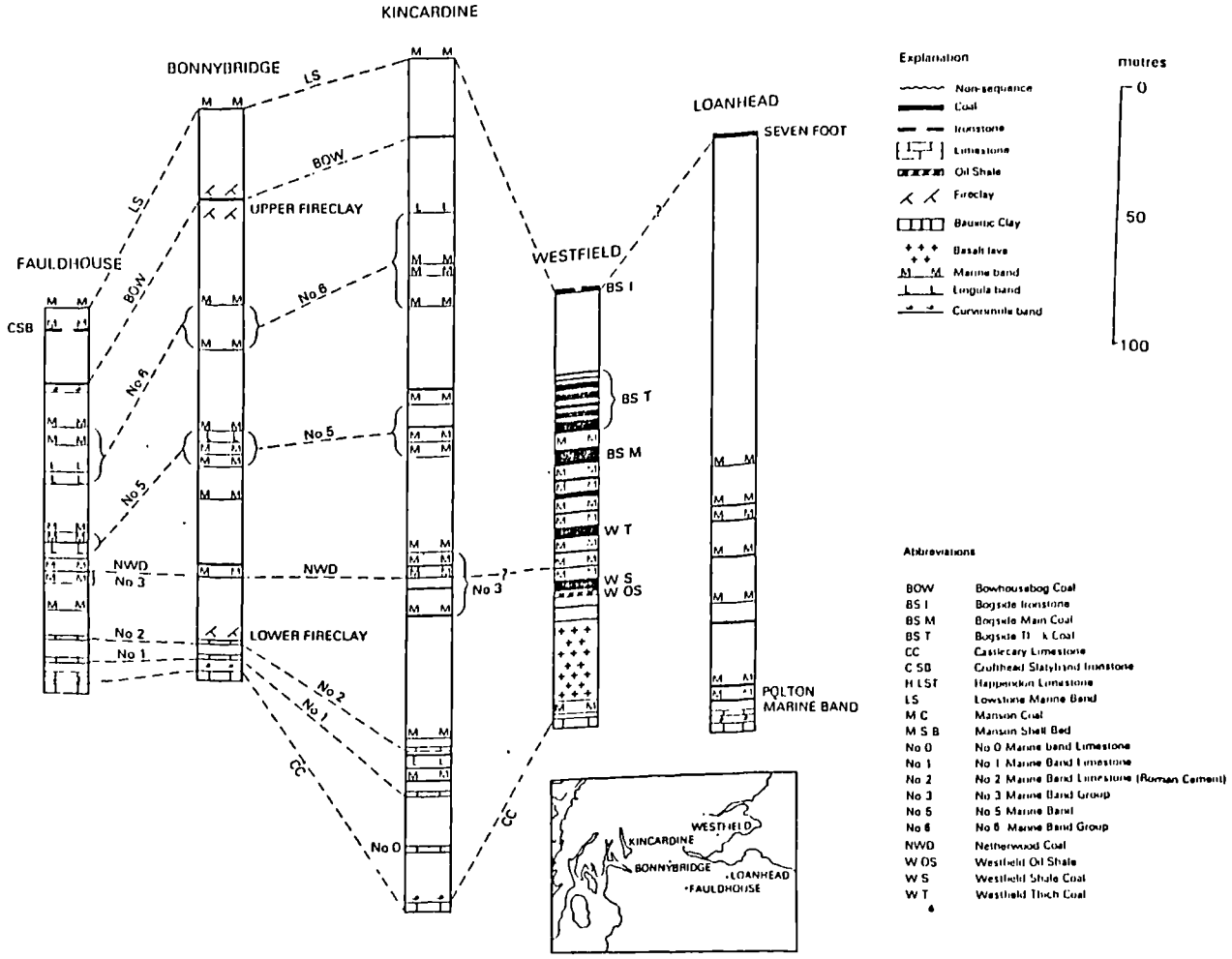


Fig.1.12a Comparative vertical successions of the Passage Group (modified from Cameron and Stephenson 1985).

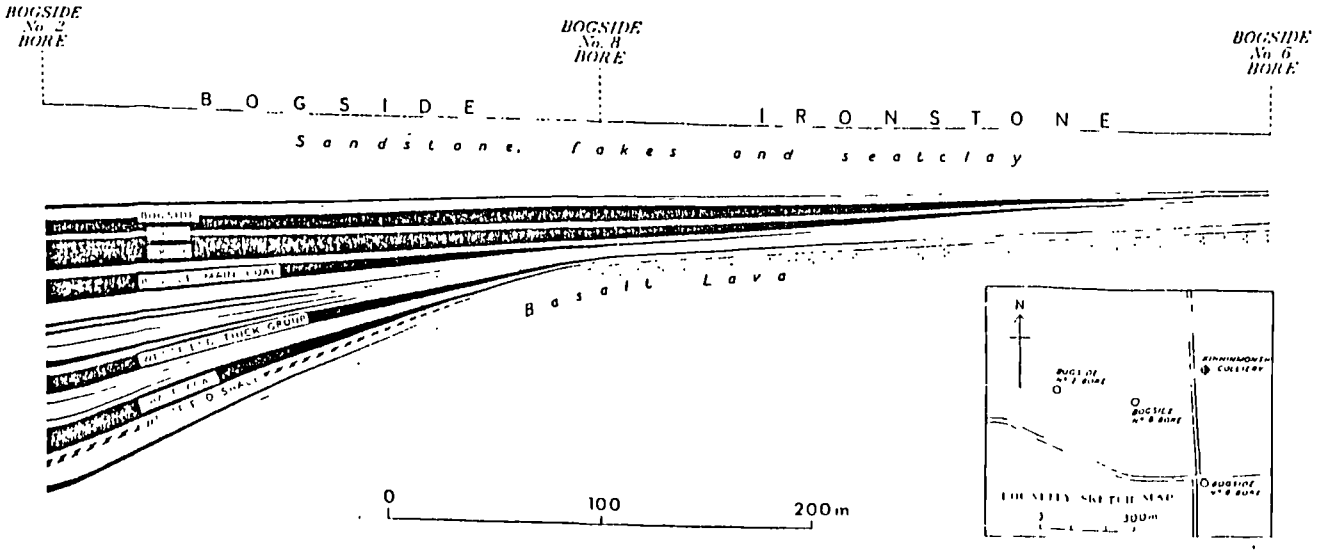


Fig.1.12b Horizontal section showing lateral variation in the Passage Group in the Westfield Basin, Fife (from Francis 1983a).

analysed in the current study. Their presence in the sequence bears witness to the submergence of the coal-forming swamps to a degree that permitted the blooming of algae in what would have been a restricted, fresh-water environment. The occurrence of at least six marine bands in the Passage Group sequence testifies to the periodic inundation of the basin by the sea.

1.4.2.3.7 Coal Measures

The Coal Measures succession in the Midland Valley is entirely of Westphalian age and is divided into the Lower, Middle and Upper units by the Vanderbeckei (Queenslie) and Aegiranum (Skipsey's) Marine Band respectively. Neither of these horizons has been found in east Fife.

As mentioned previously, the internationally accepted base of the Westphalian is not recognised in Scotland, so the local base of the Coal Measures is defined at the base of the lowest worked seam within each coalfield. Such horizons include the Lower Dysart seam in east Fife, the Seven Foot Coal of Midlothian and the Crofthead Slatyband Ironstone of the Central Coalfield. The last-named horizon is often difficult to identify beyond the type area, hence the base of the Lowstone Marine Band (only a few feet higher in the succession) is considered to be a more suitable marker for the base of the Coal Measures in the Stirling-Clackmannan and Central Coalfield Basins (Francis *et al.* 1970).

In the Lower and Middle Coal Measures (formerly the Productive Coal Measures), sedimentation patterns are generally similar to those in the Limestone Coal Group with repeated units of sandstone, mudstone, siltstone, seatearth and coal indicating that the prevailing conditions of deposition were non-marine (fluvio – deltaic). The presence of numerous coals in the sequence provides evidence for the frequent and often prolonged development of peat-swamp environments. Marine incursions were infrequent and short-lived as represented by the occurrence of several laterally impersistent marine bands, confined mainly to the upper and lower parts of the Coal Measures succession. Only twice did the sea become established over virtually the whole region, as represented by the laterally widespread Queenslie and Skipsey's Marine Bands (Brand 1977).

Following the tectonic instabilities of Passage Group times, Coal Measures sedimentation saw not only a reversion to widespread subsidence, but the diminishing influence of faults and structural highs on sedimentation. Thickness and facies variations (and seam-splitting) were still sufficiently pronounced to hinder the correlation of coal seams on a regional basis. The problem is compounded by the large number of seams in the Productive Coal Measures, at least twenty of

which are of workable thickness with many more too thin to be named. As with the Limestone Coal Group, therefore, only a few seams can be correlated from one coalfield to another (Fig.1.13).

The thickest known accumulation of Lower and Middle Coal Measures strata is in the Fife-Midlothian Basin where the sequence exceeds 500m. It has still not been established whether this basin is in fact divided into two sub-basins by the Pentland Fault (Browne *et al.* 1985).

The top of Skipsey's Marine Band marks the base of the Upper Coal Measures. The unit was formerly known as the Barren Red Measures because of the oxidation and associated reddening of strata which caused the alteration, replacement or destruction of coal seams (Mykura 1960; Francis and Ewing 1962). The main lithologies are alluvial sandstones, siltstones and clayrocks which were deposited by braided and meandering rivers on a broad floodplain (Browne *et al.* 1985). Marine influence was negligible as indicated by the scarcity of marine bands in the sequence.

The Fife-Midlothian Basin continued as a major depocentre throughout Upper Coal Measures times with over 750m of Upper Coal Measures preserved (Browne *et al.* 1985). Major accumulations also occur within the Mauchline Basin of Ayrshire where approximately 560m of strata are recorded.

1.4.3 Post-Carboniferous Sedimentation

The only post-Carboniferous sediments outcropping onshore in the Midland Valley are the red, aeolian sandstones of the Mauchline Basin, Ayrshire. They attain a thickness of approximately 450m and were deposited in an arid, desert climate.

Post-Permian strata are not represented in the Scottish Midland Valley although approximately 1800m of Mesozoic strata are preserved beneath the Tertiary flood basalts in Northern Ireland (Wilson 1986). The marked similarity between the structural styles and depositional histories of the Carboniferous basins in Northern Ireland and those in Scotland provides strong supporting evidence for the continuation of the Midland Valley rift into Ireland. It is entirely feasible, therefore, that Mesozoic strata could have been deposited in the Scottish Midland Valley. Whether the sediments were ever deposited or were removed as a result of uplift and erosion has yet to be established. Recent work suggests that the latter proposal may be more realistic. Calculations of sea-level changes dervived from the study of Quaternary sediments suggest that less than 100m of Mesozoic strata (probably Cretaceous) ever accumulated in the Scottish Midland Valley (M.A.E.Browne *personal communication*).

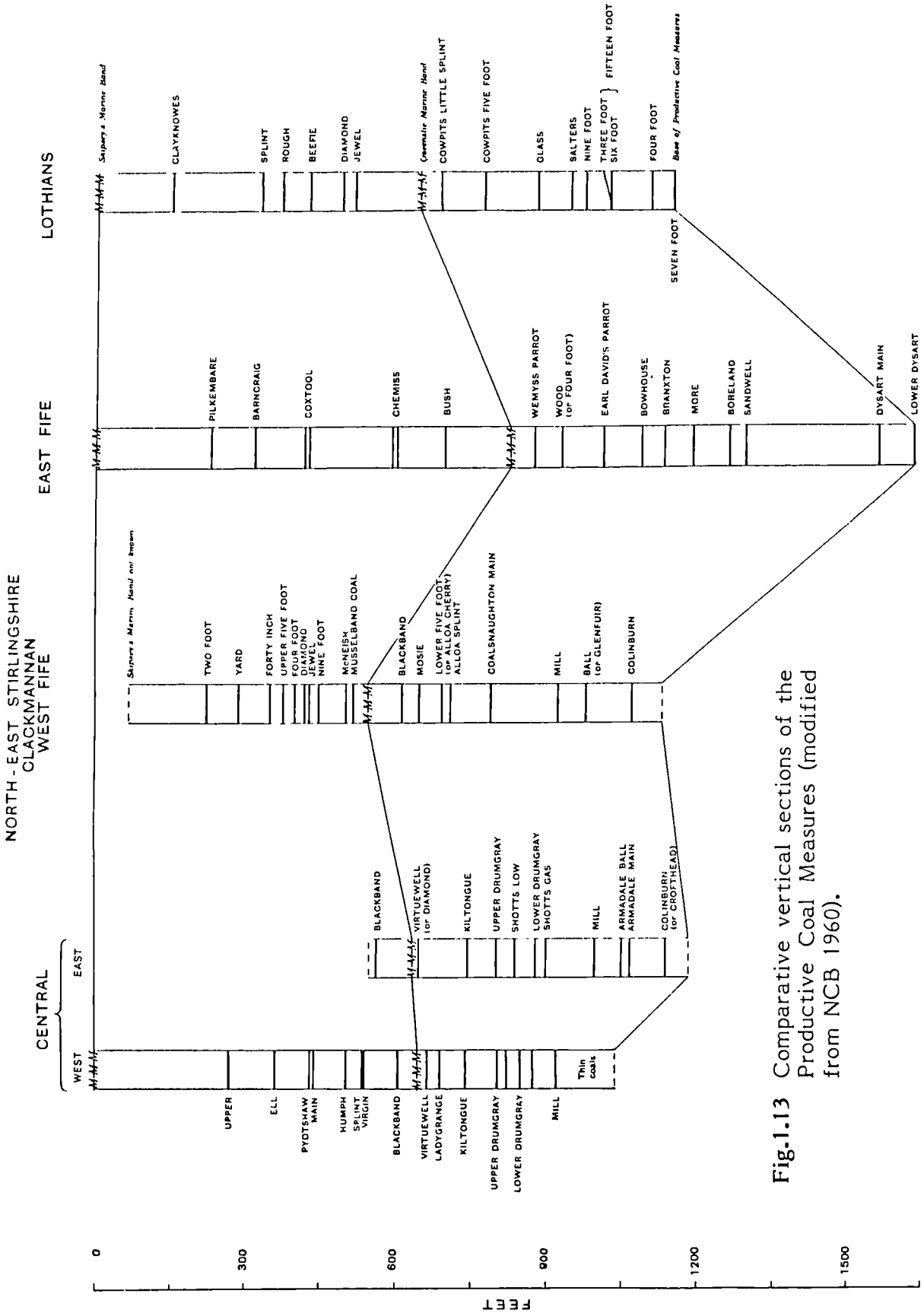


Fig.1.13 Comparative vertical sections of the Productive Coal Measures (modified from NCB 1960).

1.5 IGNEOUS ACTIVITY

Following a major period of magmatic quiescence during the Middle and Upper Devonian, the Viséan saw the onset of a major phase of igneous activity which was to continue throughout the rest of the Carboniferous period. The igneous activity was widespread spatially and temporally, with members of both the calc-alkaline and alkaline magmatic suites represented in the Midland Valley. The following sections describe the types of extrusive and intrusive igneous material encountered in the Midland Valley. Only brief details regarding the mode of emplacement are given since a more thorough evaluation of the emplacement mechanism and the nature of the sediments at the time of intrusion is given in a later chapter where the validity of opinions expressed in recent publications, along with many observations in the older literature, are reassessed in the light of organic petrological and geochemical data which were not hitherto available.

1.5.1 Extrusives

The earliest evidence for Carboniferous extrusive igneous activity in the Midland Valley is represented by the Dinantian (Viséan) Clyde Plateau Volcanic Formation which constitutes by far the greatest accumulation of volcanic rocks in the area. The lavas total some 900m in thickness and may have once covered an area of approximately 3000km^2, indicating that a virtually continuous basaltic field extended over most of the Midland Valley during Viséan times (Francis 1983b). These plateaux lavas are mainly alkaline basalts which were extruded relatively quietly from fissures and small vents, many of which display a NE-SW linear alignment inferring a structural control by underlying Caledonoid crustal lineaments. Associated pyroclastic activity is rare (Whyte and MacDonald 1974). Many of the lava flows have red boles on their upper surfaces indicating that they were subjected to subaerial oxidation. Occasional sedimentary intercalations suggest that periodic submergence of the lava pile occurred.

Lateral equivalents of the Clyde Plateau Lavas include the Craiglockhart, Arthur's Seat and Garleton Hills volcanic sequences as well as the lower part of the volcanic pile forming the core of the Burntisland Arch. This lateral continuity is assumed on the basis of the stratigraphic location of the volcanics and on geochronological determinations (Fig.1.14).

In marked contrast with the Dinantian, Silesian volcanism was almost entirely explosive in nature with eruptions typically occurring from scattered and relatively short-lived ash cones (Francis 1967). The resulting tuffaceous deposits comprise a mixture of comminuted basaltic and sedimentary debris which are

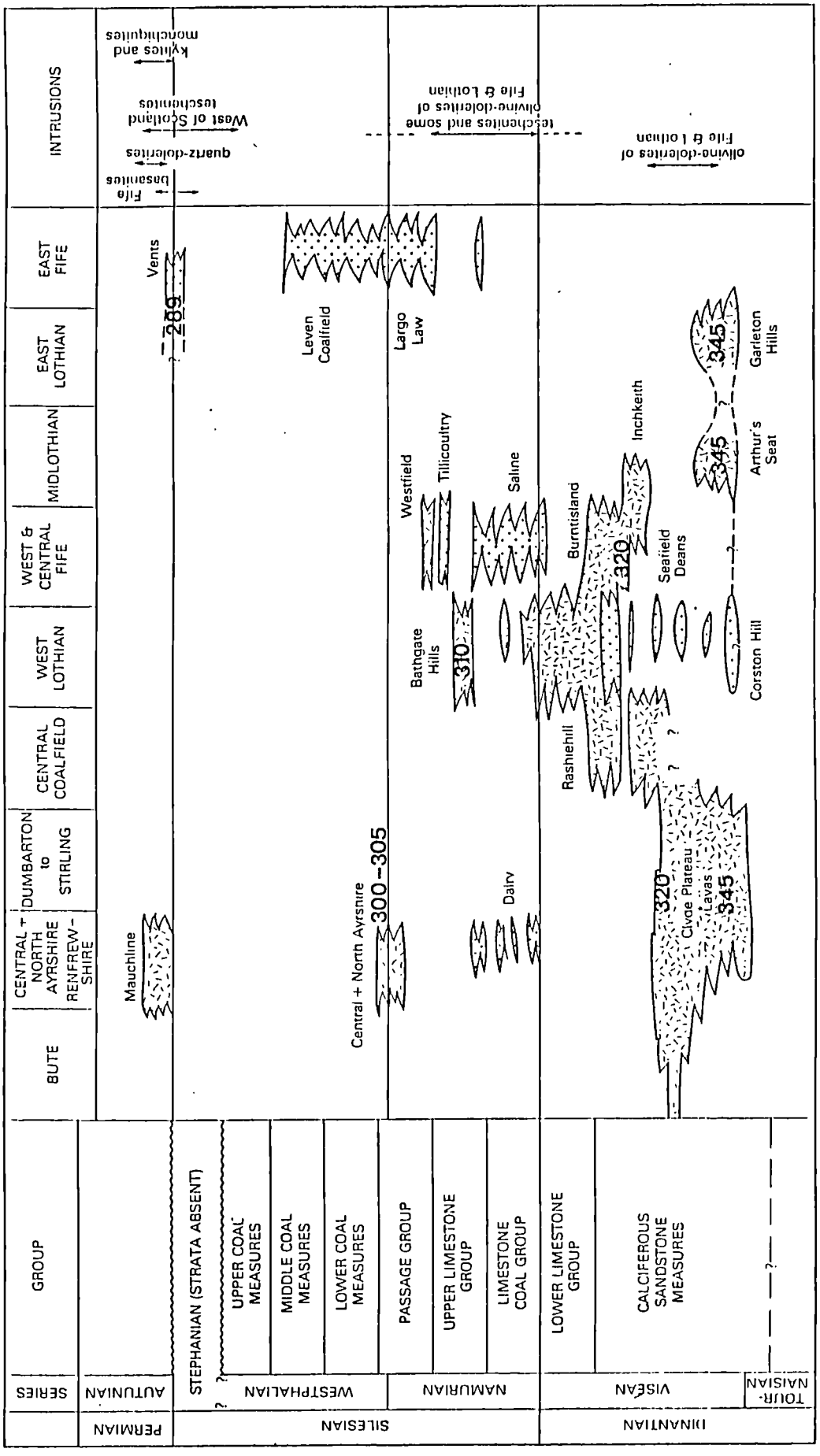


Fig.1.14 Geographical and stratigraphical distribution of Carboniferous and Permian igneous rocks in the Midland Valley (modified from Cameron and Stephenson 1985; dates from Francis1983b and Forsyth and Rundle 1977).

frequently well bedded and graded, indicating ash-fall into shallow water. The highly explosive nature of this phase of volcanicity is apparent from the scarcity of associated lavas and from the presence in the surrounding sediments of very fine tuff layers, representing fine ash fall-out, some of which has been carried for distances up to 32km from the source-vents. Subsequent kaolinisation of many tuffs has given rise to tonsteins which provide useful correlation markers (Francis 1961c, 1968a).

The principal centres for Namurian volcanic activity were in the western Midland Valley, where pyroclastic activity in the Dalry area between Limestone Coal Group and Upper Limestone Group times was followed by the late Namurian/ early Westphalian (Passage Group) lavas of Ayrshire (Richey *et al.* 1930; Mykura 1967). In the eastern Midland Valley, Namurian volcanicity occurred on a much smaller scale and was centred on three main localities. First, in west Fife, thick sequences and basaltic tuffs and agglomerates were built up over a considerable period of time from multiple vents in the Saline district (Francis 1961b). In central Fife, five pillow lava flows associated with hyaloclastites are found within the Upper Limestone Group in the Westfield Basin, whilst bedded tuffs and a few lavas of similar age to those in central Fife occur between Kirkaldy and Elie, particularly around Largo Law and Rires. Eruption from these complex volcanic centres continued into the Westphalian at which time volcanic activity, represented by tuffs and thin lava, was taking place farther to the south under the Firth of Forth (Francis and Ewing 1961).

In addition to these major eruptive centres, over a hundred smaller volcanic necks occur within east Fife alone, and much work has been devoted to the study of their field relationships, petrography and emplacement mechanisms (see Forsyth and Chisholm 1977 for a detailed review). The necks are funnel-shaped pipes containing bedded and unbedded tuffs and agglomerates which are thought to have been formed by the explosive interaction between basaltic magma and water as the former erupted either into shallow water or water-laden sediments. The structure of the necks has been modified by the inward collapse of the sediments in the pipes as well as by progressive subsidence. These phenomena were first recognised by Geikie (1902) who noticed that the vent deposits are now juxtaposed with older country rocks. Initial estimates of the extent of subsidence were of the order of 400-500m (Francis 1970), but more recent geochronological work has modified the estimates to as much as 2km (Forsyth and Chisholm 1977; Forsyth and Rundle 1977).

Most of the east Fife vents have radiometric ages of 289±10Ma (Forsyth and Rundle 1977), placing them within the Permian on the basis of the revised

Carboniferous timescale (see Leeder 1988). The youngest age determinations have been derived from intrusions cutting the Lundin Links, Coalyard and Kinaldy necks. Other contemporaneous volcanic activity occurred within the Mauchline Basin, Ayrshire, where a sequence of interbedded olivine-basalts, tuffs and agglomerates is associated with over sixty volcanic vents (Mykura 1967).

The change from the relatively quiet effusion of lavas in the Dinantian to the increasingly explosive volcanism in Silesian times has been interpreted as a function of sedimentation (Francis 1968b). In the early part of the Dinantian, continental conditions generally prevailed, and no thick sequences of sediments had accumulated. Rising magmas were therefore able to reach the surface and form extensive lava fields. The formation of thick successions in rapidly developing Silesian basins resulted in the increased build-up of poorly consolidated, water-saturated sedimentary sequences. These would have been too low in density to support the weight of ascending magma columns and would have prevented them from rising to the surface, forcing them instead to spread out as sills or sill-complexes. Subsequent piercing of the magma body by faulting, seismic activity or by an increase in internal pressure could have given rise to violent phreatic eruptions which led to the magma forcing its way to the surface through vents or pipes.

This hypothesis is supported by the close geographic and petrographic relationship between many vents and alkaline sills in the Midland Valley (particularly in Fife) and by the observation that post-Dinantian lavas commonly occur in areas where underlying sediments are thin or were undergoing uplift at the time of eruption. A change in the petrochemistry of the magma through time may also be a contributory factor. Silesian magmas were more undersaturated and volatile-rich than those in the Dinantian, properties which are frequently associated with more explosive types of eruption (Francis 1968b; MacDonald et al 1977).

1.5.2 Intrusives

Permo-Carboniferous extrusive igneous activity in the eastern and central Midland Valley was interrupted by two major intrusive episodes which resulted in the development of widespread sill complexes.

The earlier phase gave rise to the formation of alkaline-dolerite sill complexes in Fife and the Lothians (Fig.1.15). The rock types are principally olivine-dolerites and teschenites although other basic differentiates such as essexite and picrite also occur in subordinate amounts. Some minor plugs are also associated with this phase of activity. The sills attain a maximum thickness

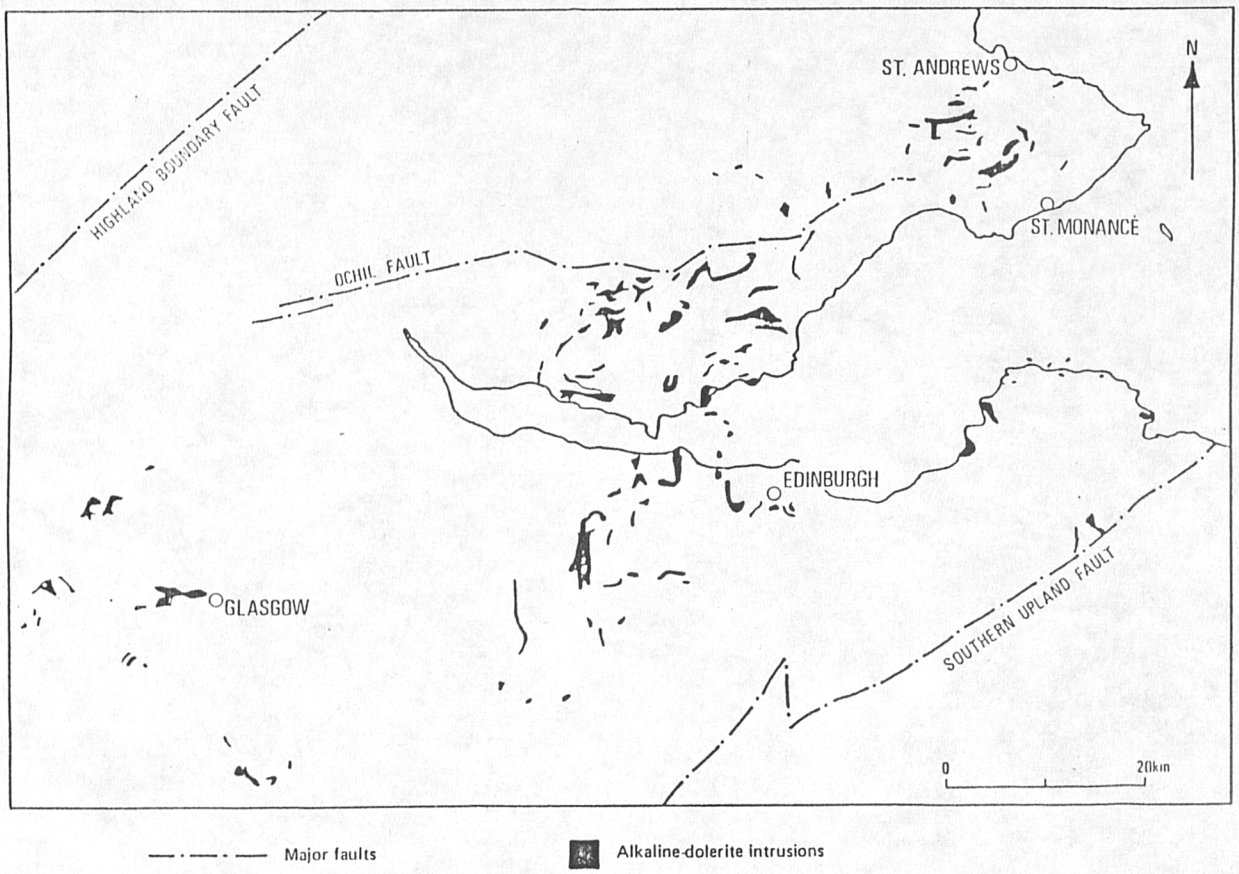


Fig.1.15 Alkaline-dolerite sills and associated intrusions of Permo-Carboniferous age in the eastern and central Midland Valley (modified from Cameron and Stephenson 1985).

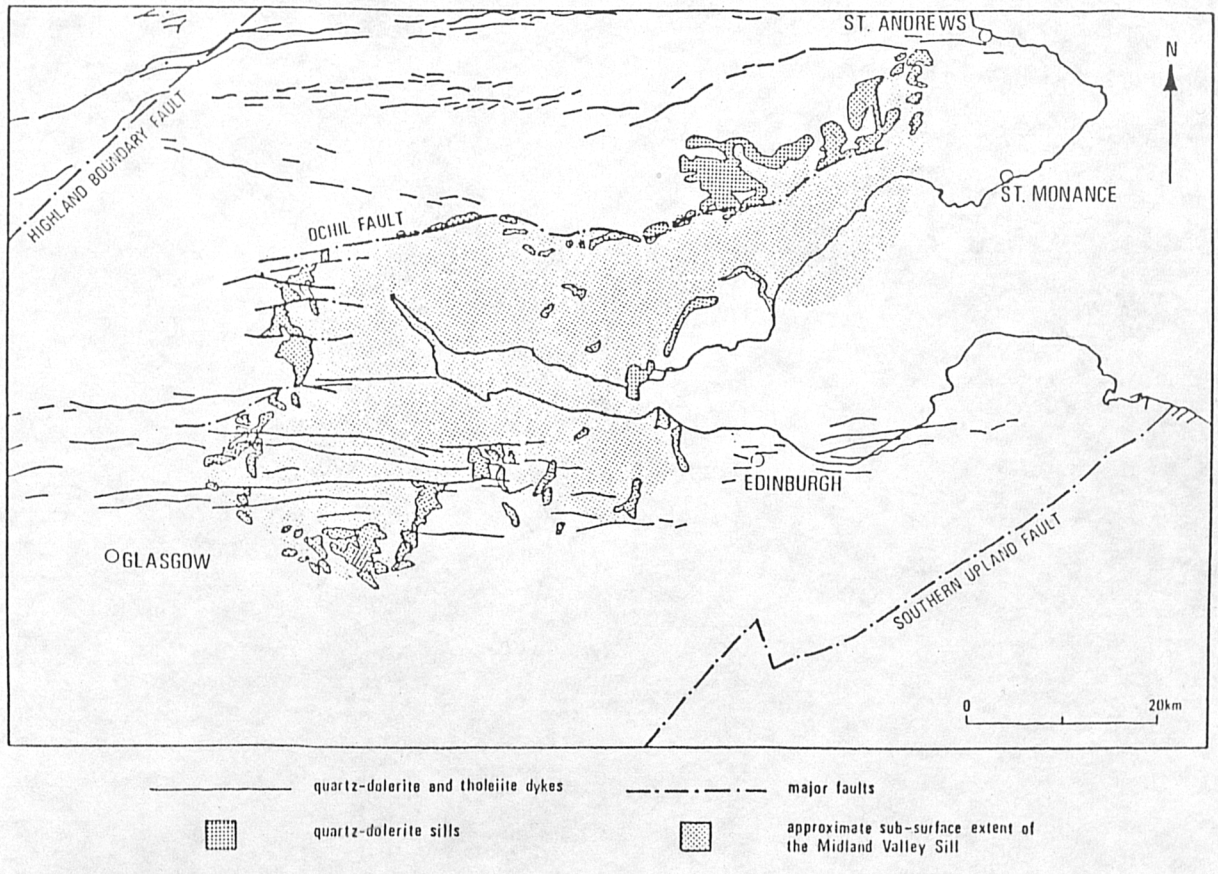


Fig.1.16 Quartz-dolerite and tholeiite intrusions in the eastern and central Midland Valley (modified from Cameron and Stephenson 1985).

of approximately 120m and penetrate strata no younger than the Upper Limestone Group. Members of this group have been radiometrically dated at 304±12Ma which, in conjunction with field evidence, suggests that the intrusions were associated with a phase of Namurian to early Westphalian magmatic activity (Forsyth and Rundle 1977). Closely associated with these intrusives are many eruptive centres through which pyroclastic material was ejected as a result of phraeomagmatic activity emanating from the roofs of the sills which, as mentioned previously, are thought to have served as high-level magma reservoirs.

Although not of comparable areal extent, an earlier series of olivine-dolerite intrusions was injected in the Lothians, and to a lesser degree in Fife, cutting mainly Calciferous Sandstone Measures strata. Very few intrusions in this suite penetrate strata higher than the Lower Limestone Group. Many potassium-argon radiometric age determinations have been hampered by argon loss, but it is thought that these intrusions were roughly contemporaneous with Clyde Plateau volcanism and therefore span the age range of 320-345Ma (De Souza 1979 and Fig.1.14).

The second widespread period of igneous activity was marked by the emplacement of a calc-alkaline province comprising quartz-dolerite sill complexes covering an area of approximately 1600km^2 in the eastern and central Midland Valley and collectively known as the Midland Valley Sill. Unlike the alkaline-dolerites, the tholeiites are not accompanied by extrusives and, furthermore, they are dissimilar in that they are closely associated with a major belt of E-W-trending tholeiitic dykes that extends beyond the areas of Carboniferous sedimentation (Fig.1.16). Many of these dykes probably acted as feeder conduits for the sills (Hinxman *et al.* 1917; MacGregor and MacGregor 1948). The sills transgress strata from the Lower Devonian up to the Westphalian Middle Coal Measures, changing horizons by a "step and chair" arrangement (Knox 1954) which is often related to pre-existing fault planes. Although attaining a maximum thickness of approximately 150m, the sills may also be present as separate leaves whose cumulative thickness has been observed to be virtually identical to the unsplit thickness (Robertson and Haldane 1937).

Radiometric age determinations of 295±5Ma for the Midland Valley Sill (Fitch *et al* 1970), coupled with petrographic and field characteristics (Walker 1935) suuggest that the Scottish sill complex is consanguineous with the Whin Sill of northern England. Both these complexes were long held to be of Stephanian age, but recent detailed geochronological work on tonsteins in central European Silesian coalfields has led to the lowering of the Permo-Carboniferous boundary, thereby placing this major phase of tholeiitic igneous activity within the Permian (Lippolt *et al.* 1984; Leeder 1988).

On the basis of the isopach maps and palinspastic reconstructions Francis (1982) and Francis and Walker (1987) have shown that the shape of the quartz-dolerite and teschenite sill complexes mirrors that of the pre-existing sedimentary basins, with intrusion thickness increasing towards the bottoms of the basins. The correspondence has been explained by envisaging that the emplacement of both igneous suites involved the gravitational, down dip flow of magma along bedding planes into syn-sedimentary basin-bottoms where it subsequently "accumulated". In the case of the quartz-dolerites, magma flow was initiated and maintained by the pressure of a head of magma represented by the upper parts of the feeder dykes, whilst volcanic pipes drilled through the unconsolidated, wet sediments provided the conduits for magma-flow within the alkaline-dolerite complexes.

In addition to the major sill complexes outlined above, other igneous intrusions in the eastern and central Midland Valley are represented by minor basinitic intrusions associated with some of the east Fife vents (Forsyth and Chisholm 1977; see previous section). In the western Midland Valley, a resumption of alkaline magmatism in the Permian gave rise to teschenitic sill complexes and other alkaline-basaltic intrusions (including dykes) which were emplaced in different phases (Francis 1983; Cameron and Stephenson 1985 and Fig.1.14).

1.6 ECONOMIC GEOLOGY

1.6.1 Coal

The longest documented interest in the commercial exploitation of resources in the Midland Valley relates to the local working of coal which was occurring as early as 1153. It was not until the eighteenth century, however, with the advent of steam power, that operations became more widespread and efficient.

Although coals are present throughout the Carboniferous succession in the area, those of a quality and thickness sufficient to render them economically viable are largely restricted to the Limestone Coal Group and the Productive Coal Measures. Valuable seams also occur in other parts of the Carboniferous sequence, the most notable of these being the Upper Hirst Coal in the Kincardine Basin (up to 2m thick) and the Passage Group coals of the Boglochty Beds which lie within the Westfield Basin (see Section 1.4.2.3.6).

Scottish coal mining reached its acme in 1913 with an output of over 42 million tonnes. The gradual working-out of seams, coupled with the increase in imports of cheaper coal from abroad, has seen the demise of the industry which, at present, is reduced to only two deep-mine sites at the Longannet Complex in west Fife and the Bilston Glen mine in Midlothian and a few opencast pits.

1.6.2 Oil Shale

In the mid-nineteenth century, oil shale rivalled coal in economic importance, and the shales were mined for over hundred years as a source of oil produced by the destructive distillation of the shale in retorts. Industrial retorting commenced in 1851 following the discovery of the algal-rich deposit, torbanite, within Lower Coal Measures strata in the Bathgate area. The localised occurrence of this thin, lenticular deposit meant that supplies were limited and so the subsequent discovery, in 1858, of oil-shale seams of much greater areal extent, within the Calciferous Sandstone Measures, led to commercial activities developing further to the east in Midlothian and West Lothian. Most of the economically viable seams, some up to 5m thick, occur within the Upper Oil-Shale Group.

Oil-shale production reached its peak in 1913, but almost collapsed in 1919 due to increased competition from abroad and the increased cost of labour. The industry was saved by a buyout by Anglo-Persian (later BP) and the merging of the largest companies. Subsequent tax concessions and improved retort designs sustained the industry until its closure in 1962 when further cost increases and foreign competition made production uneconomic. More detailed accounts dealing with the historical aspects are given by Carruthers *et al.* (1927), Stewart and Forbes (1938), Conacher (1938), Stewart (1968) and Hallet *et al.* (1985).

Renewed interest in oil shales commenced in the early 1970s following the oil crisis and current workable reserves have been estimated at 65 million tonnes (Cameron and McAdam 1978). There is no immediate prospect of these being exploited whilst North Sea production remains high.

1.6.3 Oil and Gas

Naturally-occurring oils and bituminous deposits have been known in the Midland Valley for centuries and were often considered to possess beneficial medicinal properties (cited in Howell and Geikie 1861 and Cadell 1901). Not until relatively recently has there been any systematic geological evaluation of the sources and structures associated with these hydrocarbons.

The earliest widespread hydrocarbon survey was undertaken in connection with initial attempts to investigate Britain's onshore potential shortly after the First World War. The first well to be drilled was the West Calder bore (1919) in which only traces of oil were found in an extensive volcanic sequence. Later in the same year, drilling on the southern margin of the D'Arcy-Cousland anticline (D'Arcy well) achieved some success in that fifty barrels of high quality oil were revovered from a porous sandstone horizon. Samples of this oil have been analysed and the results reported in this thesis.

Following more thorough geological investigations in the Midland Valley (Lees and Cox 1937; Lees and Tait 1945), further drilling on the D'Arcy-Cousland ridge resulted in the discovery of numerous oil and gas shows in Calciferous Sandstone Measures strata, where the oil shales and sandstones were targeted as potential source rocks and reservoirs respectively. The ensuing hydrocarbon discoveries were sufficient to enable a ten year period of oil production which ceased in 1965 after 30,000 barrels had been produced. Gas production was completed shortly afterwards, in 1967, after the flow of 330 million cubic feet, much of which had been piped to Musselburgh to supplement the town's gas supply. Sporadic drilling in the 1960s yielded further hydrocarbon shows, but no wells were commercially produced.

The rapid increase in oil prices in the early 1970s led to a resurgence of onshore-oil interest. Drilling on the Salsburgh anticline has given oil and gas shows; poor yields did not justify further development of the wells which were subsequently abandoned. More recently, success has been achieved by renewed drilling of the D'Arcy-Cousland ridge and other structures flanking the Midlothian basin. The results of analyses of hydrocarbons from the Carrington (1984) well are included in this thesis, as are the analyses of an oil and chippings from the Milton of Balgonie-1 well (1985) which was drilled on the Balfour anticline in central Fife.

From these recent drilling programmes, the indications are that any major development of oil prospects in the Midland Valley seems unlikely in the near future. Seismic surveys and structural analyses suggest that the surface simplicity of many structures belies underlying complexities, particularly at the reservoir level (Scott and Colter 1987). Furthermore, although it is clear that hydrocarbon accumulations are present in the Midland Valley, they are relatively small and are trapped in complex structures which are sporadically distributed. An additional important hindrance is that, despite the oils being of high quality, they also have a very high wax content which makes them too difficult (i.e. expensive) to produce in the current economic climate.

1.6.4 Miscellaneous

The exploitation of non-organic resources in the Midland Valley has been undertaken for many centuries and probably extends back to pre-Roman times. The main objectives were precious metals located in veins, mainly lying within the Lower Devonian volcanics of the Ochil Hills and the Clyde Plateau Volcanic Formation of the western Midland Valley. Other metalliferous ores associated with this phase of ?Caledonian mineralisation were subsequently worked and include ores of copper, zinc, lead, barium and nickel.

Ferrous minerals also played a major part in the economic development of the area, with the bedded ironstones (claybands) providing the major sources of ore during the rapid growth of the iron and steel industries in the eighteenth century. These bedded ores are most abundant within the Limestone Coal Group and Coal Measures sequences, and the iron is present mainly in the form of siderite (MacGregor *et al* 1920). The organic-rich ironstones (blackbands) were particularly valuable as the presence of organic matter meant that they were self-calcining and therefore reduced smelting costs.

In addition to metallic ores, the lithological diversity within the Midland Valley succession resulted in the utilisation of a variety of deposits, mainly from the Carboniferous sequence. Limestones, sandstones, igneous rocks and gravel have all been used in the construction industries whilst peat has been used for agricultural purposes and domestic burning. The hydrogeological properties of many Upper Devonian and Carboniferous sandstones make them good aquifers (Browne *et al* 1985, 1987), and some local water supplies have been drawn from suitable horizons.

More detailed accounts and further references relating to the economic growth and development of the Midland Valley may be found in the publications of Duff (1983) and Cameron and Stephenson (1985).

CHAPTER 2

ORGANIC MATTER IN COALS AND SEDIMENTS

2.1 INTRODUCTION

The characterisation of carbonaceous matter in the geosphere embraces two fundamental analytical disciplines *viz.* organic petrology and organic geochemistry. The optical analyses are almost exclusively directed towards the study of the organic fraction which is insoluble in common organic solvents, termed kerogen, which frequently accounts for more than 90% of the organic matter in coals and sediments. In the context of the current project it is ironic that this term was first used in connection with sediments from the Midland Valley, where it was proposed to describe the oil-yielding organic material in the Lothians oil shales (Crum-Brown, cited in Carruthers *et al.* 1912, p.143).

Semi-quantitative and quantitative measurements on the various kerogen components in transmitted, reflected and fluorescent light enable valuable assessments of the amount, type and maturity of organic matter. Not only is the optical approach rapid, relatively simple and inexpensive, a further significant advantage is its ability to allow the delineation of non-indigenous and reworked materials.

Geochemical evaluations entail the study of the amount and composition of the soluble organic fraction or bitumen which may, in part, be equal to "petrological bitumen". Although providing valuable information on source materials, maturity, correlation and migration paths, a major drawback of the study of extractable organic matter (EOM) is that the data are derived from a bulk analysis of a relatively small percentage of the total organic matter from which it is often difficult to delineate readily the contributions from oil- and gas-prone material within a mixed kerogen-type. It is also invariably difficult to recognise the extent to which external contaminants or reworked matter have modified the geochemical signature.

In considering the relative merits of organic petrology and organic geochemistry, which have been outlined in several publications (e.g. Brooks 1978; Heroux *et al.* 1979; Tissot 1984; Bayliss 1985; Murchison 1987), and despite the ever-increasing number of analytical procedures available to the organic geo-scientist, it is apparent that there is no one organic analysis which is universally applicable in accurately and completely characterising organic matter. A multi-technique approach has therefore been adopted in the current project so as to yield the maximum amount of information on the amount, type and rank of the organic matter in the Midland Valley. A brief review of organic petrological and geochemical principles and diagnostic parameters is presented in the following sections, with particular emphasis placed on those that bear most relevance to the work undertaken in this study.

2.2 ORGANIC PETROLOGY

2.2.1 Organic-Matter Types and Coalification

Coals represent the richest accumulations of terrestrial organic material in the geosphere and consist of a diverse array of plant debris in varying states of preservation. The individual components which contribute towards the heterogeneity of coals are termed macerals, a definition first proposed by Stopes (1935) to describe the microscopically discernible organic components in coals. Maceral classification is carried out according to the International Committee for Coal Petrology's (ICCP) standardised Stopes-Heerlen nomenclature (ICCP 1975) which is periodically revised. Three major maceral divisions are recognised on the basis of reflectance, colour, morphology and relief. The divisions and their constituent macerals are shown in Table 2.1 along with inferred progenitors and their mode of preservation/incorporation.

Maceral group	Maceral	Origin
Vitrinite	Telinite	Humified plant remains typically derived from woody, leaf or root tissue with well to poorly preserved cell structures
	detro-Collinite	Humified attrital, or less commonly detrital, plant tissue with particles, typically being cell fragments
	telo-Collinite	Humified material showing no trace of cellular structure, probably colloidal in origin
Liptinite	Sporinite	Outer casings of spores and pollens
	Cutinite	Outer waxy coating from leaves, roots and some related tissues
	Resinite	Resin filling cells and ducts in wood: resinous exudations from damaged wood
	Fluorinite	Essential oils in part; some fluorinite may be produced during physico-chemical coalification and represent non-migrated petroleum
	Suberinite	Cork cell and related tissues
	Bituminite	Uncertain but probable algal origin
	Alginite	Tests of some groups of green algae; material referred to alginite shows moderate to strong fluorescence
	Exsudatinite	Veins of bitumen-related material expelled from organic matter during coalification
Inertinite	Fusinite	Pyrofusinite—originates from wood and leaf tissues in forest fires
	Semifusinite	Wood or leaf tissues weakly altered by mouldering or by biochemical alteration
	Intertodetrinite	Similar to fusinite or semifusinite but occurring as small fragments
	Macrinite	Humic tissue probably first gelified and then oxidized by processes similar to those producing semifusinite
	Sclerotinite	Moderately reflecting tissue of fungal origin—largely restricted to Tertiary coals
	Micrinite	Largely of secondary origin and formed by disproportionation of lipid or lipid-like compounds to fluid hydrocarbons and a high reflecting granular residue of micrinite

Table 2.1 Maceral terminology and origins (modified from Murchison 1987).

Although the high concentration of organic matter in coals makes them a prime choice for studies in organic petrology, the seams themselves comprise only a relatively small part of sedimentary sequences. Dispersed grains of coaly material, however, are virtually ubiquitous, having been incorporated in sediments

through the normal sedimentary cycle. Studies by Bostick (1973, 1974) and Alpern (1976) have confirmed that these grains or phytoclasts undergo the same thermal metamorphism as coals, therefore coalification studies may be accomplished in areas bereft of seams or in successions where coals are not available for sampling.

The process of coalification is irreversible and is the means by which the agencies of temperature, pressure and time act on accumulations of plant matter, converting them to lignites, sub-bituminous and bituminous coals and eventually to anthracites and finally graphite. Although this transformation represents a continuum, it may be subdivided into two major stages, a biochemical stage and a geochemical stage. The biochemical stage is largely instrumental in establishing coal type and the main processes involve humification and gelification. These are important modifiers of the physical characteristics of coal, bringing about a reduction in water content, an increase in density and a decrease in porosity of the original plant material.

The geochemical stage of coalification is largely responsible for the imposition of rank and mainly involves chemical changes which cause an increase in the ordering of the molecular structure of the various macerals. The main operative processes are condensation, aromatisation and defunctionalisation, the net result being a continuous, but non-linear, carbon-enrichment of the macerals with increasing rank (M. and R.Teichmüller 1968).

The simplest and most widely accepted chemical classification of the macerals is based on elemental composition and the construction of van Krevelen diagrams (van Krevelen 1961 and Fig.2.1).

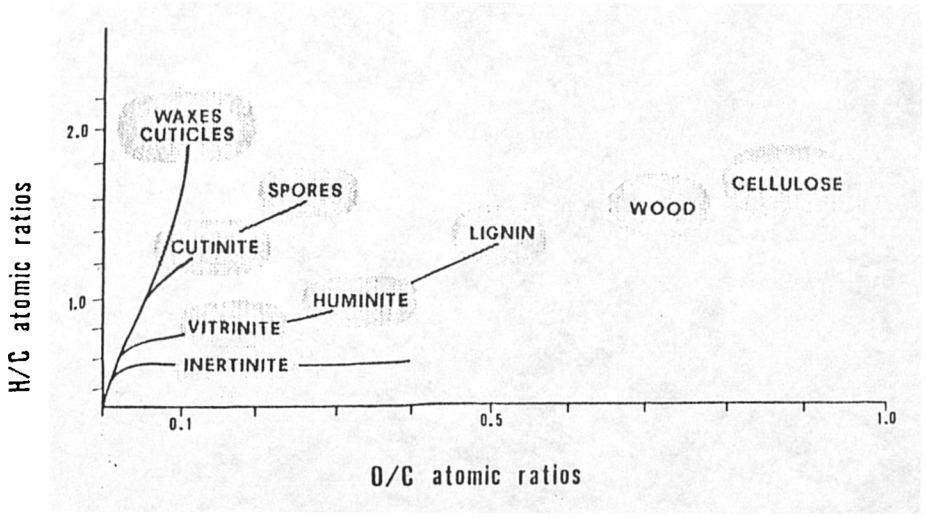


Fig.2.1 Selected plant and coal materials and their positions in the van Krevelen diagram (from Tissot and Welte 1984).

The different maceral groups respond differently to the coalification process and "evolve" along different pathways which eventually converge as coalification progresses.

2.2.2 Kerogen Types and their Source Potential

The van Krevelen-type classification was adopted by geochemists to classify dispersed, insoluble organic material (kerogen) in sediments (Forsman 1963; McIver 1967; Tissot *et al.* 1974). Four kerogen types are currently recognised and are classified as follows:-

Type I kerogens are characterised by high initial H/C ratios (c.1.5+) and low O/C ratios (<0.1). Much of the material is highly aliphatic in nature, consisting of long, saturated hydrocarbon chains with very few polyaromatic and heteroatomic components. This kerogen type is represented by algal-rich matter that has accumulated mainly within lacustrine environments. Such a high liptinitic content is considered to have resulted either from the selective accumulation of algal material or from the severe degradation of non-algal matter during deposition.

Type II kerogens comprise organic matter with relatively high initial H/C ratios (c.1.0-1.5) and relatively low (<0.2) O/C ratios. Volumetrically, it is the most important kerogen type with respect to petroleum generation. Although type II kerogens contain some aliphatic material (mainly medium-length chains), cyclic structures assume a much greater importance than in type I kerogen .Type II kerogens are generally associated with marine, reducing environments in which the precursor organic materials were planktonic organisms and microbes.

Type III kerogens have a low initial H/C ratio (less than c.1.0) and a high initial O/C ratio (c.0.2-0.3). Polyaromatic nuclei and heteroatomic compounds are the predominant chemical species, whilst aliphatic groups are generally subordinate but, when present, indicate a contribution from plant waxes. Type III kerogen is derived from terrestrial plant debris which may accumulate *in situ* or may be carried into lacustrine or marine environments.

Type IV kerogens were originally defined by Harwood (1977) to describe a kerogen type which possesses abnormally low H/C ratios (c.0.5-0.6) and very high O/C ratios (c.0.2-0.3). It contains an abundance of aromatic nuclei and oxygen-containing groups, but no aliphatic chains. This kerogen type can be derived from any organic precursors, which may be recycled from older sediments or have been heavily altered by weathering, combustion and biological oxidation in swamps prior to burial.

The evolution paths of type I, II, III and IV kerogens are broadly analogous to the coalification tracks of the maceral groups alginite, sporinite, vitrinite and inertinite respectively. For types I, III and IV, the comparisons are acceptable since the elemental compositions of the kerogens are comparable with those of their inferred algal and humic precursors. In the case of type II kerogen however, such a correspondence is not so clear-cut. Implications that a sediment plotting along a type II evolution path is genetically linked with exinitic material is often without foundation; type II kerogens have invariably been bio- and geochemically degraded resulting in them becoming amorphous in appearance, contrasting with spores and exines which tend to retain their morphological integrity in the sedimentary environment. Furthermore, much dispersed type II organic matter is deposited in marine environments in which contributions from exinitic materials are generally very small.

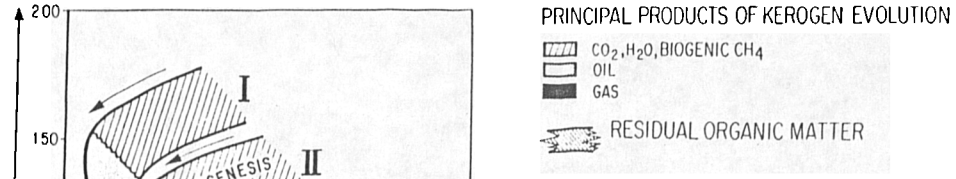
It has often been considered that amorphous kerogen is equivalent to sapropelic organic matter and has, by inference, been derived from oil-prone type I or type II materials. This assumption is highly misleading : not only can amorphous organic matter arise from the chemical and physical degradation of any primary type of organic matter (Rogers 1979; Batten 1983), studies have shown that the resulting elemental composition of amorphous kerogens is highly variable and can spread over the entire field of a van Krevelen diagram (Durand and Monin 1980; Powell *et al.* 1982). This spread may arise through the varying degrees of preservation and degradation of the organics and/or through the presence of mixed kerogen types in the sample. Although many amorphous kerogens do in fact plot along a type II evolution path, it has been demonstrated that they do not necessarily show a good potential for hydrocarbon generation (Powell *et al.* 1982; Sentfle *et al.* 1987; Hartman-Stroup 1987).

As coalification progresses, kerogens lose functional groups, accounting for the principal variation in O/C ratios, and release liquid and gaseous hydrocarbons which are largely responsible for the variation in H/C ratios. The remaining kerogen is correspondingly enriched in aromatic carbon so that it moves towards a state of thermodynamic equilibrium, represented by the three-dimensional structure of graphite.

A general scheme of kerogen evolution has been proposed by Vassoevich *et al.* (1969) and Tissot *et al.* (1974), based on changes in elemental composition and hydrocarbon generation (Fig.2.2).

Three successive stages of organic maturation are distinguished:-

Diagenesis, marked by a decrease of O/C ratio, generation of carbon dioxide, water, heavy heteroatomic compounds and some biogenic methane;



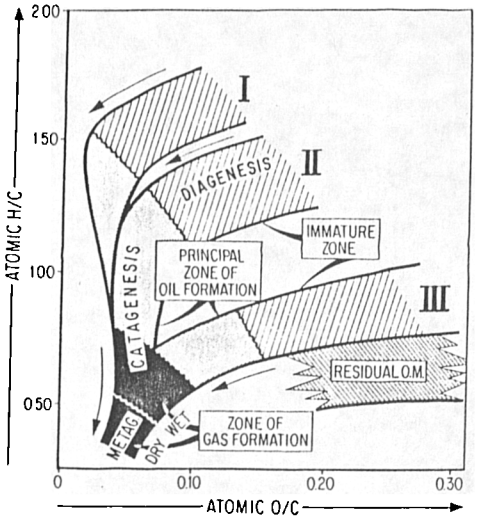


Fig.2.2 General scheme of kerogen evolution presented on van Krevelen's diagram. The successive evolution stages are indicated and the principal products generated during that time (modified from Tissot and Welte 1984).

Catagenesis, corresponding to the main zone of oil and gas formation and represented by a decrease of H/C ratios and the maximum generation of liquid hydrocarbons;

Metagenesis, the stage of hydrocarbon cracking and gas generation, represented by further decrease of H/C ratios and generation of gas, mainly methane, by the cracking of previously formed oil and also of remaining kerogen.

The nature and relative amounts of the various generated hydrocarbon products depend upon the type of organic matter, its degree of thermal evolution and its position on the coalification track. Type I kerogens yield highly paraffinic or paraffinic-naphthenic oils, reflecting the predominantly aliphatic nature of the algal source material. Type II kerogens give rise to naphthenic-paraffinic to aromatic-naphthenic oils and comprise the greatest global compositional category of crudes (Tissot and Welte 1984). The source potential of terrestrial organic matter is variable and is related to the proportion of hydrogen-rich components present. Although liptinitic macerals may have H/C ratios similar to type II organic matter at immature stages (Tissot *et al.* 1974), the H/C ratios of much terrestrial matter is usually lower due to the mixing of humic and liptinitic components. The relatively low H/C of vitrinite is inimical to the production of significant quantities of liquid hydrocarbons, these being predominantly aromatic in character, reflecting the structural configuration of the humic precursors. The higher hydrogen content of cuticles, spores and pollens is more conducive to the generation of liquid hydrocarbons and gives rise to high-wax oils (Hedberg 1968). A high proportion of the waxy material may also originate from the bacterial biomass through direct input as a consequence of extensive microbial reworking of the humic substrate (Powell 1984).

The resinous components of coals have also been shown to possess significant potential for sourcing liquid hydrocarbons, giving rise to naphthenic oils (Snowdon 1980; Snowdon and Powell 1982). The hydrocarbon-generation threshhold is achieved at much lower maturation levels than for other types of organic matter due to the highly labile nature of resinite.

The exceptionally low H/C ratio of type IV (inertinite) kerogen has long been taken to preclude any possibility that hydrocarbon formation could occur from this kerogen type; indeed this material is often referred to as "residual" or "dead" carbon. In recent years however, the inertness of type IV kerogen has been questioned. In determining the reflectance properties of different macerals throughout the rank range, Smith and Cook (1980) found that the reflectance of inertinite increased more rapidly than that of vitrinite in the range 0.2 to 0.9%Rv. This was taken to imply the concomitant release of at least some hydrocarbon products from inertinite and led to the suggestion that "its dynamic coalification path makes the name inertinite a misnomer". Some inertinites have also been found to be reactive in hydrogenation processes indicating the presence of chemical groupings capable of generating hydrocarbons (Mitchell *et al.* 1977; Steller 1981; Evans *et al.* 1984).

The presence of liquid and gaseous hydrocarbons in some Australian sequences in which the maceral assemblages are almost entirely inertinitic leads, in the absence of other evidence, to the inference that the only possible source for the hydrocarbons could be intertinite (Smyth 1983). As a corrollary from the deductions of Cook (1986), in relation to the source potential of vitrinites, it is conceivable that, although the H/C ratio of inertinite is *per se* very low, the sheer volume of this material in many successions may be sufficiently great to offset the "normal" requirement of a high initial H/C ratio for hydrocarbon generation. Many deep, inertinite-rich and areally extensive Australian basins may therefore possess considerable petroleum potential. Some Australian inertinites have been shown to fluoresce (Diessel 1985) indicating the presence of oil-prone organic matter, but the possibility that this is due to the absorption of migrating hydrocarbons cannot be excluded.

2.2.3 Oil Shales

There have been many attempts to classify and define oil shales, based on such criteria as chemical and physical properties (Mott 1951), organic-matter type (Bitterli 1963; Combaz 1974), mineralogical content (Down and Himus 1940), depositional environment (Bitterli 1963; Duncan 1974) and industrial use of the oil product (Ozerov and Polozov 1969). No one method has achieved

universal acceptance; indeed many of the definitions and parameters have proved to be too academic, conflicting or generally inconclusive. A more practical approach for defining the term "oil shale" has been, and still is, related to oil yield. In general terms, an oil shale is any rock which yields commercial quantities of oil upon destructive distillation. The precise definition will obviously depend on economic criteria and currently, yields of less than 25 litres per tonne are considered non-viable (Tissot and Welte 1984). A liptinite content of 10% is considered to be the minimum required to exceed this economic threshhold (Sherwood 1984; Cook 1988).

As the nature of the liptinitic components exerts an important control on oil-shale quality and the type of hydrocarbon product released, much work has been directed towards the study of this maceral group. For many decades the major hindrance in elucidating these components has been the limitation of the long-established transmitted- and reflected-light microscopical techniques in resolving hydrogen-rich macerals and other bituminous materials from each other and from the mineral matrix. The advent of fluorescence microscopy (van Gijzel 1961, 1966,1967, 1975) proved to be a major step forward in the delineation of oil-prone materials and provided a significant impetus for the development and refinement of a detailed classification of oil shales. The most widely employed system today is based upon the work of Hutton *et al.* (1980) and Cook *et al.* (1981) with recent modifications by Hutton (1987). These workers use a genetic classification of oil shales based on the type of organic matter present. In addition to being rapid, relatively simple and cheap, their classification scheme is attractive in that it enables petrographic data to be related to the chemical composition of oil shales and shale oils and gives an insight into depositional environments and the commercial potential of the deposits. It also retains many of the old petrological terms. This genetic scheme and its associated terminology have been followed in this thesis. Six major groups of oil shale are currently recognised:-

(i) **Torbanite** or boghead coal. This material has long been established as an algal-rich deposit and derives from accumulations of the green, colonial algae *Pila* and *Reinschia*. The *Pila* form is considered to be equivalent to the extant, freshwater, planktonic alga *Botryococcus braunii* (Zalessky 1926; Blackburn and Temperley 1936). The precise botanical affinities of *Reinschia* have not been firmly established although some authors maintain a genetic relationship with *Botryococcus* (Blackburn and Temperley 1936; Dulhunty 1944; Combaz 1974). In this thesis the term torbanite is reserved for sediments containing a minimum of 90% (vol) of *Botryococcus*-related algae

(Cook 1988), thus corresponding with the petrographic characteristics of the type deposit at Torbanehill (Blackburn and Temperley 1936; Skilling 1938). Deposits with at least 50% of *Botryococcus*-related algae are termed torbanitic shales or torbanitic coals, depending on the nature of the associated materials. Depositional environments of torbanites were fresh- to brackish-water lakes of restricted areal extent which were closely associated with peat swamps (Conacher 1917; MacGregor 1938; Moore 1968). Torbanites therefore tend to be relatively thin, lenticular bodies which are invariably interbedded with, or pass into, coal seams.

(ii) **Kukersite.** This oil shale comprises abundant remains of the colonial marine algae *Gloeocapsomorpha prisca*. Deposits of this type are rare, the most intensively studied examples originating from the type area of Estonia.

(iii) **Tasmanite.** This accumulation is characterised by the dominance of the tests of the punctate unicellular marine alga *Tasmanites* which is deposited in shallow- to brackish-water environments. The fossil algae in this oil shale are closely related to the living genus *Pachysphaera pelagica*.

(iv) **Lamosite.** As defined by Hutton *et al.* (1980) and Cook *et al.* (1981), this term refers to laminated oil shales of lacustrine origin which contain abundant lamellar or filamentous algal material known as lamalginite. The lamalginite has been further subdivided by Hutton (1987) according to whether the lamellae are discrete, thin-walled entities (<0.5mm long) or whether they form layered or anastomosing sheet-like structures, some or all of which may be degraded. These divisions are known as discrete lamalginite and layered (or continuous) lamalginite respectively. Discrete lamalginite may originate from a variety of precursors, the most common of these in Tertiary sediments being the freshwater green algae *Pediastrum*, *Septodinium* and *Cleistosphaeridium* (Hutton 1987; Cook 1988). The precise precursor(s) of the sheet-like, layered lamalginite are difficult to ascertain, but its morphology, coupled with its intimate association with the mineral matrix observed in many samples suggests an origin from mat-forming Cyanophycae (Hutton *et al.* 1980; Sherwood *et al.* 1984; Hutton 1987).

(v) **Marinite.** This category is used by Hutton (1987) to describe oil shales in which the principal liptinite is discrete lamalginite derived from pelagic marine precursors such as dinoflagellates and acritarchs. (N.B. Marinite is equivalent to the term "marosite" of Cook 1988). Marine oil shales containing two or more co-dominant liptinite macerals are referred to as "mixed oil shales". These may also contain variable amounts of humic matter (Cook *et al.* 1981).

(vi) **Cannel Coals.** Liptinite-rich cannels (and canneloid shales) may have high oil yields and therefore fall within the definition of oil shale given earlier. The liptinite is mainly derived from vascular plants, although minor contributions from algae (usually *Botryococcus*) can also occur. Cannel coals accumulate in bogs and peat swamps and, together with torbanites, comprise a division of terrestrial organic matter known as the sapropelic coals. Unlike the humic coals which usually contain less than 10% liptinite and were deposited as peats, the sapropelic coals comprise the biological and physical degradation products of contemporaneous peat swamps and contain at least 10% liptinite. They were laid down as subaquatic, organic-rich muds in peat-swamp pools (Moore 1968). Although air- and water-borne accumulations of liptinite may account for the selective concentration of some hydrogen-rich components, thereby enhancing the oil potential of these deposits, the main agency responsible for the oil-proneness of the sapropelic coals is the anaerobic degradation of cellulosic organic matter, leading to the relative enrichment of hydrogen-rich material. It is conceivable that some of the resulting sapropelic ooze-like matter could permeate the remaining humic materials, leading to the formation of perhydrous vitrinites which are most commonly associated with sapropelic coals (Kröger 1968; Stach *et al.* 1982).

From the preceding account it is evident that there are many types of algal material contributing to oil shales. These may be divided into two major groups based on morphology. Discrete, elliptical or disc-shaped algal bodies, such as those characterising torbanite, tasmanite and kukersite are termed telalginite. The bodies may be colonial or unicellular, they are generally thick-walled and invariably show distinct external structures. They display strong fluorescence at low ranks. Finely lamellar or filamentous algal matter is grouped as lamalginite (regardless of depositional environment) which is derived from unicellular or thin-walled, colonial planktonic or benthonic algae. Lamalginite generally shows little recognisable structure in sections perpendicular to bedding and fluoresces less intensely than telalginite. Telalginite and lamalginite correspond with the terms alginite A and alginite B respectively, of Hutton *et al.* (1980). The first two, more descriptive, terms are used in this thesis. A summary of oil-shale characteristics, depositional environments and presumed precursors is shown in Fig.2.3.

	TERRESTRIAL OIL SHALE		LACUSTRINE OIL SHALE			MARINE OIL SHALE	
Lithotype	CANNEL COAL	TORBANITE	LAMOSITE		MARINITE	TASMANITE	KUCKERSITE
			RUNDLE TYPE	GREEN RIVER TYPE			
Precursor Organisms	VASCULAR PLANTS	GREEN ALGAE	GREEN ALGAE	?BLUE-GREEN ALGAE	GREEN ALGAE ACRITARCHS DINOFLAGEL-LATES	GREEN ALGAE	GREEN ALGAE
Growth Form	VARIOUS	PLANKTONIC COLONIAL	PLANKTONIC COLONIAL UNICELLULAR	BENTHONIC ALGAE? ALGAL OOZE	PLANKTONIC UNICELLULAR	UNICELLULAR	PLANKTONIC COLONIAL
Dominant Maceral/ Constituent	SPORINITE RESINITE CUTINITE	TELALGINITE	LAMALGINITE	LAMALGINITE	LAMALGINITE BITUMINITE	TELALGINITE	TELALGINITE
Known Precursors	Angiosperms Gymnosperms	Pila Reinschia	Pediastrum Septodinium Cleisto-sphaeridium	?	Nostocopsis	Tasmanites Leiosphaer-idium	Gloeocapso-morpha prisca
Related Organisms	Various Extant Vascular Plants	Botryococcus braunii	Pediastrum	Extant Blue-Green Algae	Various Extant Algae Acritarchs Dinoflagellates	Pachysphaera pelagica	Botryococcus braunii
Environment of Deposition	Peat Swamp	Lacustrine (in a Peat Swamp)	Fresh to Brackish Lake	Stratified or Saline Lake	Marine	Shallow Marine	Shallow Marine

Fig.2.3 Oil-shale classification (modified from Hutton 1987).

2.2.4 Microscope Techniques and Principles

2.2.4.1 Reflected-Light Microscopy

2.2.4.1.1 Optical Properties of Vitrinite

Reflected-light microscopy finds its greatest application in the differentiation of the humic constituents vitrinite and inertinite and in providing an accurate measure of the rank (maturity) of organic matter. To overcome the problem of the inherent heterogeneity of coals, it is essential that comparative rank studies are made using only one petrographic constituent. Vitrinite is best suited for this purpose for several reasons:-

(i) it is the most abundant maceral;

(ii) it is relatively homogeneous;

(iii) it is distributed in many facies;

(iv) it is readily identified;

(v) its reflectance increases more uniformly throughout the rank range than does the reflectance of any other maceral; and

(vi) it does not suffer retrograde metamorphism.

These factors, coupled with the ease, accuracy and precision of the measuring procedure, have made vitrinite reflectance probably the most satisfactory and certainly the most widely used optical parameter for determining the rank of coals and organic matter in sediments. Reflectance, however, is not a fundamental property of matter since its value depends upon the refractive index of the measuring medium. The fundamental optical parameters of matter are the refractive index and the absorption index, which can be derived from reflectance measurements made in two media of different refractive index.

As coalification proceeds, modifications in the chemical structure of vitrinite are reflected by changes in the refractive and absorptive indices and hence in reflectance. Physical modification to the molecular structure of vitrinite occurs in response to an increase in unidirectional confining pressure exerted by overlying strata. On a molecular level, the pressure increase leads to the progressive alignment of the aromatic lamellae to give a preferred orientation which is expressed by the increased development of optical anisotropy. A quantitative evaluation of anisotropy is given by measuring the bireflectance, determined by taking the numerical difference between the maximum and minimum reflectances, the orientations of which are described below.

Vitrinite may be envisaged as a pseudocrystalline material normally possessing a uniaxial negative indicatrix with the optic axis perpendicular to the bedding (Fig.2.4).

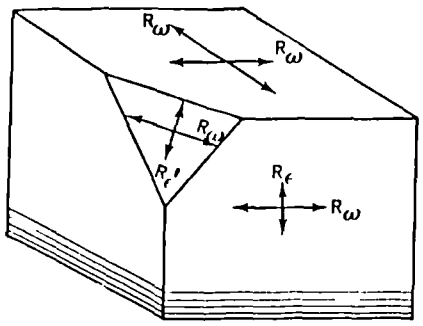


Fig.2.4 The anisotropic character of vitrinite. The range in reflectance in polarized light is dependent on the orientation of the polished surface with respect to the bedding. R_ω and R_ϵ are the maximum and minimum reflectances, respectively. R_ϵ', an apparent minimum reflectance, is intermediate between R_ω and R_ϵ. (Adapted (from Davis 1978).

Under these circumstances:-

(i) a surface cut perpendicular to the bedding will exhibit maximum reflectance when the incident light is polarised parallel to the bedding and a true minimum reflectance when polarised perpendicular to it;

(ii) a surface cut parallel to the bedding displays maximum reflectance in all directions since this section corresponds to the circular section of the reflectance ellipsoid; and

(iii) an oblique cut will show a true maximum parallel to the bedding and an apparent minimum perpendicular to it.

The difference between the maximum and minimum reflectance increases with increasing rank, becoming most noticeable beyond reflectances of $\bar{R}_v max(oil) = 1.30\%$ (Fig.2.5). The increase in bireflectance can be envisaged as being analogous to an increase in the ellipticity of the reflectance indicatrix.

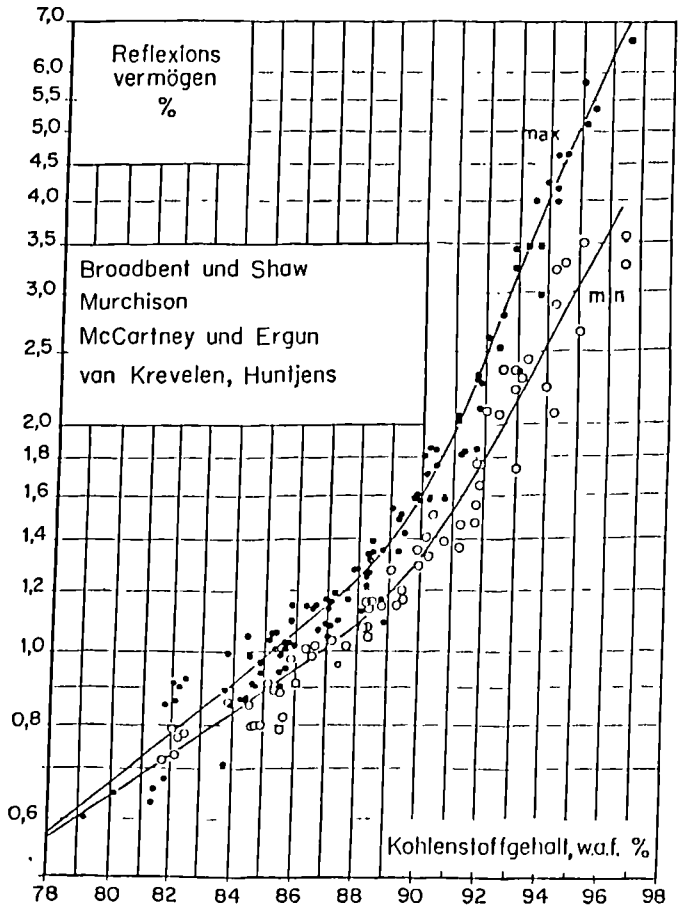


Fig.2.5 Relationship between rank and reflectance (from ICCP Handbook 1971).

With coal samples, the maximum reflectance can be obtained by rotating any coal particle until the stratification is parallel to the plane of vibration of the polarised incident light. The determination of true minimum reflectance, however, necessitates the use of samples which are oriented perpendicular to the bedding so that on one revolution of the microscope stage two reflectance maxima and two minima will be recorded, corresponding to the principal directions of the vitrinite indicatrix. For dispersed organic matter in sediments, the small size of vitrinite clasts hinders rotation, as the phytoclasts often tend to move away from the measuring aperture on rotation of the microscope stage. This defect has led to the use of "random" or "average" reflectances when readings are taken

on unoriented samples using a fixed-stage position with the polariser out of the optical train (random) or in the optical path (average). Maximum reflectances can be calculated from average reflectances using the formula of Hevia and Virgos (1977):-

$$\%R_o av = \frac{2\,Ra + Rc}{3}$$

where Ra and Rc are, respectively, the maximum and minimum reflectance in the principal directions of the vitrinite.

2.2.4.1.2 Modification of the Optical Properties of Vitrinite and Causes of Anomalous Vitrinite Reflectance Values in Geological Environments

2.2.4.1.2.1 Development of Biaxial Vitrinite

Although vitrinite is conventionally regarded as behaving analogously to an optically negative uniaxial material, departures from this state have been reported. Jones *et al.* (1973) showed that vitrinite in coal scares apparently became increasingly biaxial in character as the angle between the scare and the enclosing sedimentary bedding increased. This biaxicity was attributed to the effects of overburden pressure gradually distorting the highly ordered molecular structure of the vitrinite as the scare showed an increased departure from parallelism with the host bedding.

Instances of biaxicity have been recorded in high-rank coals. Dahme and Mackowsky (1951) noted the existence of significant bireflectance in the plane of the bedding of an anthracitic vitrinite, whilst Cook *et al.* (1972) found that some Welsh anthracites developed biaxicity. Several possible causes were advocated in the latter study, including tectonic stress, internal strain and remnant botanical-form anisotropy. Increasing variations in reflectance minima, as well as reflectance maxima, were observed in vitrinites from sediments approaching the contact of the Midland Valley Sill and Whin Sill (Raymond 1983), and were inferred to be a consequence of the development of biaxial vitrinites due to the presumed distortion of the vitrinite matrix in response to severe thermal stress.

Tectonic stress is a further factor promoting the formation of biaxial vitrinites. Their occurrence has been correlated with stress fields induced by faults (Stone and Cook 1979) and with regionally developed fold structures (Hower and Davis 1981; Levine and Davis 1984). These studies have shown that the identification of the orientation of the planes of maximum and minimum reflectance can help to unravel different phases of tectonism.

2.2.4.1.2.2 Effect of Host-Rock Lithology

The nature of the enclosing sediment has an important influence on the development of optical properties of organic matter in both coals and sediments. Damberger (1965, 1966, 1968) showed that thick sandstone and conglomerate horizons are associated with small coalification gradients. Comparable observations were made by Jones *et al.* (1972) who demonstrated that coal seams roofed by shales attained a higher rank than those roofed by more arenaceous rocks.

Bostick and Foster (1975) investigated the influence of host rocks using phytoclasts. They discovered that the reflectance of vitrinite in different lithologies taken from a narrow stratigraphic horizon displayed considerable variation. Not only were reflectance values of sediments usually much lower than those of the associated coals, vitrinites from sandstones displayed significantly lower reflectances than those derived from shales or limestones. Many of the data, however, were not entirely conclusive.

Perhaps the strongest evidence to date demonstrating the significant control that host-rock lithology exerts on the optical properties of vitrinite derives from the work of Pearson (1988). In studying numerous borehole reflectance profiles from coal-bearing sequences in northeast England, he has shown that, although there is generally a considerable scatter of reflectance values from seams covered by argillaceous roofs, the reflectances of seams covered by arenaceous sediments are consistently lower than the regression line drawn for the reflectances of vitrinites with argillaceous roofs. The values often plot more than one standard deviation from the regression line. Furthermore, a detailed investigation of the reflectances of a coal seam overlain by both sandstone and shale roofs in the same colliery workings showed that the reflectance of the coal underlying the sandstone is significantly lower than when overlain by a shale roof (Pearson 1988; Pearson and Murchison 1989).

Although the previous studies have clearly shown the lithological dependency of vitrinite maturation, no one explanation can yet unequivocally account for the variations in reflectance outlined above. Reflectance fluctuations in interbedded sandstone and shale sequences have most commonly been ascribed to differences in thermal conductivities of the two sediments (Damberger 1965, 1966, 1968; Jones *et al.* 1972; Pearson 1988). Argillaceous sediments have lower thermal conductivities and porosities than arenaceous rocks enabling the former to act as insulators, thereby prolonging the duration of heating of closely associated organic matter. It has also been proposed that the easier escape of volatiles from arenaceous lithologies could have accentuated vitrinite reflectance differences in interbedded sandstone and shale sequences (Jones *et al.* 1972).

An alternative cause of the anomalously low reflectance values encountered in coals overlain by sandstones in paralic sequences has recently been attributed to redox potential (Fermont 1988), which exerts a major control on the microbial communities within coal swamps. It has been suggested that the low reflectance values associated with sandstones result from more intense biodegradation of cellulosic precursors during early diagenesis, when microbial activity was enhanced by influxes of nutrient-rich, oxygenated water. Under these conditions, the residual organic matter would be more oxygen-depleted which will consequently lead to lower reflectance values. Higher reflectance values are inferred to be associated with vitrinites which have not been so severely biodegraded due to coverage by a stagnant watermass. The vitrinite precursors will therefore remain relatively oxygen-rich, ultimately yielding a higher-reflecting vitrinite. Differences in redox potential have also been invoked by Wenger and Baker (1987) to account for the occurrence of low-reflecting vitrinite in black, organic-rich phosphatic shales which are juxtaposed with calcareous grey shales that display much higher vitrinite reflectance values. Their conclusions are diametrically opposed to those of Fermont in that the black shales are thought to have experienced a more anoxic diagenetic history, resulting in the retention of vitrinite which is more hydrogen-rich than that in the adjacent calcareous shales which have undergone a more oxic diagenesis. Palaeoenvironmental factors related to oxicity were also considered important in explaining reflectance variations in some New Zealand coals (Newman and Newman 1982).

Whatever the cause for lithologically-induced reflectance deviations, the obvious corrollary from the foregoing account is that the most meaningful results are likely to be gained from determinations which are restricted to a single lithology. This course was followed as far as possible in the current study.

2.2.4.1.2.3 Association with Liptinitic Macerals

It is now widely recognised that the presence of large quantities of liptinitic macerals in coals and sediments can significantly modify the optical properties of vitrinite by causing reflectance suppression. Taylor (1966) was one of the first workers to identify this phenomenon by noting that vitrinites displaying anomalously low reflectances also had submicroscopical liptinitic particles incorporated within their matrices. Later work showed that vitrinites from sapropelic coals had much lower reflectance values than those from adjacent humic coals (Kunstner 1976), presumably reflecting the more oil-prone nature of the sapropelic coals mentioned previously. Subsequent work has shown that vitrinite reflectance

suppression may arise through an association with resinous components (Ting 1977), alginite (Correia and Connan 1974; Hutton and Cook 1980; Hutton *et al.* 1980; Wolf and Wolff-Fischer 1984) or in fact any assemblage of oil-prone materials (Kalkreuth 1982; Price and Barker 1985), including migrated hydrocarbons (Jones and Edison 1978). The suppression effect has been reported to persist up to reflectance levels as high as 4.00%, as determined on "normal", optically-unaltered vitrinites (Price and Barker 1985).

In the first attempt to quantify the degree of reflectance suppression, Hutton and Cook (1980) noted that an increase in the percentage of alginite in the Australian, Joadja torbanite was accompanied by a decrease in reflectance of vitrinite. Additional data from other torbanites confirmed the previous results (Hutton *et al.* 1980) and a causal relationship between the abundance of alginite and the reflectance of vitrinite was inferred, probably related to the liberation of aliphatic hydrocarbons from the alginite and their subsequent absorption into the vitrinite structure. Similar deductions have been made from other studies, and although the precise mechanism is not known, the current consensus is that reflectance suppression is due to the incorporation of hydrogen-rich substances into the vitrinite matrix. These substances may either be released from juxtaposed liptinitic macerals and/or oil-prone amorphous matter or may be derived from external, migrated hydrocarbons. It is clear that, if maximum use is to be made of reflected-light microscopy, the possibility of lowered reflectances must be borne in mind when examining material from liptinite-rich sequences. The suppression phenomenon therefore highlights a major problem of the vitrinite reflectance technique which, if unrecognised or disregarded, could lead to erroneously low estimates of sample maturity.

2.2.4.1.2.4 Effect of Pressure

Pressure brings about major changes in the physical nature of coals, particularly in the low-rank stages, but relatively little attention has been directed towards its role in effecting chemical and therefore optical changes in vitrinite.

Early work by M. and R.Teichmüller (1949, 1950) and Huck and Patteisky (1964) established that pressure retarded coalification by hindering the release of volatiles, but only relatively recently is the effect of pressure receiving much credence as a significant cause of anomalous vitrinite reflectance values in geological environments. McTavish (1978) has demonstrated that in temperature versus reflectance plots, a significant improvement in correlation and a reduction in scatter is observed when pressure is taken into consideration because of its important role in influencing the thermal conductivity of strata. Perturbations in heat flow caused by the presence of abnormally

pressured zones have also been invoked to explain major kinks in vitrinite reflectance gradients from wells in North America (Law *et al.* 1989).

2.2.4.2 Fluorescence Microscopy

The low reflectances of liptinite macerals mean that, when viewed in reflected light, they show little optical contrast with each other or with clay minerals. This is particularly the case in low-rank samples and was, for a long time, the major factor hampering the development of a satisfactory and widely applicable oil-shale classification. With the development of fluorescence microscopy however, the range, morphological diversity and properties of liptinitic macerals and other hydrogen-prone materials have been elucidated in great detail.

Under blue-light or ultraviolet-light excitation, liptinitic macerals may be characterised by their morphology, fluorescence colour and fluorescence intensity. The fluorescence colour changes with increasing rank by showing a progressive shift towards longer wavelengths which is accompanied by a reduction in fluorescence intensity. These changes have been quantified by many workers, and spectral fluorescence measurements on palynomorphs have been successfully used as rank parameters (van Gijzel 1971; Ottenjann *et al.* 1974, 1975). The spores change in colour from green in the peat/lignite stages (up to $cR_oav=0.30\%$) through yellow (up to $cR_oav=0.45\%$) to orange ($cR_oav=0.90\%$) and finally to red ($cR_oav=1.30\%$), after which they cease to fluoresce. As with reflectance determinations, spore-fluorescence characteristics are influenced by palaeoenvironmental factors, e.g. redox potential, degree of microbial activity etc. (Teichmüller and Wolf 1977). Different plant species also invariably display marked variations in their fluorescence properties at a given maturity level as defined by other indices (van Gijzel 1961, 1975). Comparative studies must therefore be restricted, if possible, to spores from the same species.

Sporinite fluorescence is most useful at the lower end of the maturation scale where it finds its greatest use as a complementary maturation parameter to vitrinite reflectance. In this region, maturation indices based on spore fluorescence show greater rates of increase relative to vitrinite reflectance in low-rank coals and sediments, when accurate vitrinite reflectance determination may also be markedly affected by type influences and suppression effects.

Although spectral fluorescence equipment (permitting quantitative evaluations) was not available during the course of this project, observations under blue-light excitation were undertaken to complement those made in reflected light. Spore-fluorescence colour and intensity provided an independent, albeit semi-quantitative, assessment of rank whilst the amount, type and state of preservation

of liptinitic macerals (and other hydrogen-rich matter) gave valuable information on source potential and depositional environments.

2.2.4.3 Transmitted-Light Microscopy

Transmitted-light microscopy affords the best means for discriminating between structured humic and liptinitic macerals and amorphous matter. The difficulties inherent in the preparation of thin sections of carbonaceous materials, coupled with the rise in absorption and therefore decreasing translucency of organic matter with increasing rank, have resulted in the almost exclusive use of strew mounts in transmitted-light studies. This method involves concentrating the kerogen components by using the standard palynological technique of digesting the mineral matrix with hydrochloric and hydrofluoric acid and then strewing the organic components on a glass slide. Subsequent viewing of the strew mounts in transmitted light enables the organic components to be distinguished on the basis of translucency and morphology. The juxtaposition of microfossils and tissue remains means that transmitted-light microscopy is well suited to the interpretation of depositional environments and the construction of palynofacies.

Although maturity information may be gained from this method, by observing the level of thermally-induced spore discolouration (Staplin 1969, 1977), no such assessments were made in this project as standards were not available. Transmitted-light microscopy plays a subordinate role in this study and was mainly employed in an attempt to gain more information on the types of algae contributing to lamosites and other organic-rich rocks.

2.2.5 Optical Characteristics of Heat-Affected Organic Matter

2.2.5.1 Thermally-Altered Organic Matter in Geological Environments

Since the Carboniferous succession in the Midland Valley is riddled with extrusive and intrusive igneous rocks, it is inevitable that this thesis should include a study of at least some aspects of the igneous-induced transformation of insoluble and soluble organic matter. A brief resumé of the thermal effects observed under geological and laboratory conditions is therefore deemed relevant. Thermal alteration under both circumstances contrasts markedly with the normal coalification process since the latter develops on a regional scale and involves a much slower response to "normal" crustal temperature gradients, rather than a relatively rapid response to localised concentrations of heat. Furthermore, the organic matter does not pass through its decomposition point in normal coalification which it does do during rapid thermal metamorphism in nature and during carbonisation.

The thermal alteration of coals in nature is readily observed in contact aureoles where it is often possible to trace the progressive alteration of a completely unaffected coal away from the intrusion, to highly altered coal (sometimes natural coke) adjacent to the igneous body. Many publications have dealt with the thermal alteration of coals in the natural environment, a phenomenon first alluded to in the work of Sinclar (1672) who observed that an intruded coal was "so dried that it moulders on handling it". Over two centuries later, widespread interest in heat-affected coals was stimulated by the economic implications of whether igneous activity could improve or impair the quality of potentially workable coals. Early work was largely confined to observations on the extent of burning, loss of volatile matter and change in the chemical composition of the coals (Taylor 1854; Heslop 1889; Dumble 1899; Stanley 1908; McFarlane 1929; Hinxman *et al.* 1920; Briggs 1935). More thorough evaluations of the changes brought about by intrusives were not forthcoming until optical examination of coals was performed in transmitted (Ueji 1932; Marshall 1936) and reflected light (Marshall 1945; Seyler 1948; Stach 1952). Optical studies have subsequently been undertaken in many localities worldwide where results from earlier work have been confirmed and expanded (Brown and Taylor 1961; Chandra 1963; Johnson *et al.* 1963; Chatterjee *et al.* 1964; Bogdanova *et al.* 1964; Kisch 1966; Kisch and Taylor 1966; Crelling and Dutcher 1968).

Two of the more recent accounts detailing the optical and textural modifications occurring in organic matter subjected to thermal metamorphism are given by Creaney (1977) and Jones and Creaney (1977) who described the detailed petrographic changes occurring within a coal in the aureole of the Collywell Bay dyke, Northumberland. Briefly, the first effects are the slight vesiculation of liptinitic macerals and the development of elliptical vesicles in vitrinite perpendicular to the bedding. This coincides with the onset of softening in the vitrinite, which then increases in plasticity to such a degree that the bedding is distorted and eventually destroyed. The evolution of volatile matter becomes more violent, inducing shattering to give a microbreccia which anneals itself on further heating. The vitrinite then shows renewed, coarser vesiculation and develops a granular mosaic, at which point it may be regarded as a natural coke. These changes are accompanied by an exponential increase in vitrinite reflectance. Many of the optical and morphological features encountered in progressing towards the Collywell Bay dyke have also been recognised in heat-affected sediments approaching sills in the Northumberland Trough and the Midland Valley (Raymond 1983; Raymond and Murchison 1989), suggesting that the characteristics described above in relation to coals can also be applied to dispersed organic matter in sediments.

The width of the various zones described above and the total distance over which the influence of heat will be felt are governed by properties of both the intruding and intruded rock. In the former case, these will include intrusion thickness, duration of magmatic emplacement, rate of flow, degree to which it has already crystallised, nature and amount of associated volatiles, temperature, chemical composition and intrusion mechanism. Important properties of the country rock include its petrographic composition, initial rank of its organic matter at the time of intrusion, thermal conductivity, volatile content, degree of development of fissures and cleats and the pressures and temperatures operative prior to and during intrusion. The exact petrographic constitution of any thermally-affected coal or sediment will be the result of a complex interplay between these factors, all of which will vary in different geological provinces.

Some of these variables have been incorporated in the mathematical formulae of Lovering (1935) and Jaeger (1957, 1959, 1964) in an attempt to model patterns of heat flow associated with intrusive igneous activity. Criticism is often levelled at these models for their failures to account adequately for the latent heat of crystallisation, but they are, nevertheless, considered to provide reasonable estimates of the order of magnitude of thermal events, at least in lithified sediments. As Gretener (1981, p.60) has pointed out, where intrusions invade porous, water-saturated sediments, the existing models are not likely to be reliable as there are too many variables associated with cooling effects due to the vapourisation and convection of pore-water which have never been fully characterised.

2.2.5.2 Laboratory Carbonisation and its Geological Implications

To gain an insight into the molecular changes occurring during thermal metamorphism in nature, comparable reactions in the form of carbonisation experiments have been undertaken. It must be borne in mind, however, that the simultaneous recreation of all geological conditions in the laboratory has not yet been realised. Many of the fundamental results which carry implications for geological studies derive from the work of van Krevelen (1961), Taylor (1961) and Brooks and Taylor (1965). Additional important constraints were provided by Goodarzi (1975), following an extensive series of heating experiments in which the effects of many variables on the optical and textural characteristics of vitrinite were investigated. The main aspects of the carbonisation process and the petrographic characteristics of the products have been reviewed by Murchison (1978).

The carbonisation process is essentially one of polymerisation and aromatisation and can be divided into three main stages as shown in Fig.2.6.

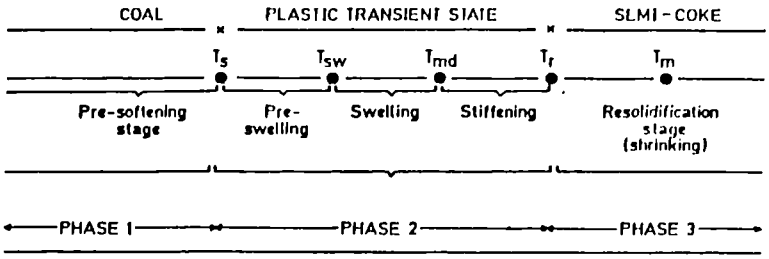


Fig.2.6 Important temperature levels during the carbonization process at which changes in state occur. T_s is the softening temperature, T_{sw} the temperature of initial swelling, T_{md} the temperature of maximum devolatilization rate, T_r the resolidification temperature, and T_m the onset of molecular reorganization in the solid. (Modified after van Krevelen 1961.)

The changes in each phase can be characterised as follows:-

Phase 1 c.150°C-400°C. Characterised by "molecular stripping": some condensation reactions: little effect on optical properties.

Phase 2 c.400°C-650°C. Phase of active decomposition: extensive devolatilisation and condensation reactions: severe molecular disruptions: fluidisation with major effects on optical properties.

Phase 3 c.650°C-1500°C. Resolidification: crystallographic changes in the solid state.

It is phase 2 which is crucial to the formation of mosaic textures since the change of state allows for a much greater molecular mobility which is essential for the development of a high degree of molecular ordering. Whilst in this fluid condition, an optically anisotropic mesophase, in the form of droplets, develops from an originally isotropic matrix. Each droplet represents a zone of aromatic lamellae whose orientation is everywhere normal to the sphere surface, and with increasing temperature these coalesce to form a granular mosaic.

Variations in the length of each phase and the temperature at which they develop are produced by modifying any of the following factors: residence time, heating rate, maximum temperature attained during heating, particle size, pressure, degree of oxidation, rank and type of organic matter. It is the last three parameters which are fundamental controls on the development of mosaics in coal macerals so that in general:-

(i) vitrinites of coals lower than bituminous rank, severely oxidised vitrinites and inertinitic macerals do not form mosaics;

(ii) vitrinites in the high- to medium-volatile bituminous-rank range with vitrinite reflectances of c.0.80%-1.20% soften so that the particles agglomerate into a coherent mass: insufficient plasticity prohibits these caking coals from forming a granular mosaic;

(iii) vitrinites and liptinites of bituminous-rank coals containing c.87%-89% carbon and with vitrinite reflectances of c.1.30%-1.50% will become sufficiently fluid to allow the formation of excellent mosaics; and

(iv) anthracitic vitrinites (R_o>c.2.00%) will not form mosaics.

These results have important implications for interpreting thermal histories in geological environments: the presence of mosaiced vitrinites in sedimentary successions indicates that the organic material had attained a medium- to low-volatile bituminous rank *prior* to the igneous event which resulted in mosaic formation. It should be noted, however, that in laboratory carbonisation experiments, mosaics may be produced from high-volatile bituminous vitrinites under very high heating rates (Goodarzi and Murchison 1978). The incidence of mosaic textures, when used in conjunction with other optical characteristics of coals and sediments, can therefore provide a valuable means of solving geothermal problems by placing constraints on the timing of thermal events with respect to regional coalification (Ridd *et al.* 1970; Creaney 1977, 1980; Raymond 1983).

2.3 ORGANIC GEOCHEMISTRY

2.3.1 Organic Richness

A measure of organic richness of a sample is given by the total organic carbon (TOC) content which is determined by combusting the organic carbon to carbon dioxide after carbonate carbon has been removed by acid treatment. The minimum concentration of organic carbon required to make an effective source rock has been empirically determined as 0.5% (Ronov 1958) although most of the world's oil accumulations are associated with source rocks which have TOCs greater than 2.5%.

The classification of organic richness shown in Table 2.2 is adopted in this thesis, based on the guidelines utilised by several service companies.

Table 2.2 Classification of Organic Richness

TOC %	Richness
0.1-0.5	Lean
0.5-1.0	Fair
1.0-2.0	Good
>2.0	Rich

2.3.2 Extractable Organic Matter (EOM)

As referred to previously, the sedimentary organic fraction which is soluble in common organic solvents is termed bitumen. This fraction represents the total amount of hydrocarbons, resins and asphaltenes in a sample and is expressed either as ppm or more commonly as mg of extract per gram of organic carbon (mg/gTOC). The latter usually ranges from approximately 20mg/gTOC in immature samples to c.200mg/gTOC in samples within the peak hydrocarbon generation phase. Values decrease to c.10mg/gTOC in the zone of metagenesis due to cracking of liquid hydrocarbons into gaseous products.

Parameters derived from the fractionation of EOM can also be used to gain information on the type and maturity of organic matter. The hydrocarbon yield, usually expressed in mg/gTOC, increases from c.10mg/gTOC in immature sediments to c.50-120mg/gTOC at the peak of oil generation. The saturate to aromatic ratio also increases with increasing maturation due to the cracking of side chains on aromatic nuclei (Tissot *et al.* 1971; Tissot and Welte 1984). The ratio is also type-dependent: it is higher, for a given rank, in aliphatic-rich type I organic matter than in organic matter dominated by humic material.

Service company guidelines for the classification of rocks based on EOM in the diagenetic/early catagenetic stages are given in Table 2.3.

EXTRACTABLE ORGANIC MATTER		EXTRACTABLE HYDROCARBONS		CLASSIFICATION
ppm of sediment	mgEOM/gTOC	ppm sediment	mgHC/gTOC	
< 500	50	< 100	10	Poor
500-1000	50-100	100-200	10-20	Fair
1000-2000	100-200	200-500	20-50	Good
> 2000	> 200	> 500	> 50	Rich

Table 2.3 Source-rock classification based on soluble-extract data at a maturity of $\leq$0.50% vitrinite reflectance.

2.3.3 Biological Markers

In studying the detailed constitution of extractable organic matter, particular emphasis has been placed on the identification of biological markers. These are compounds present in the geosphere whose structural configuration suggests an unambiguous link with a known natural precursor. The term was first coined by Speers and Whitehead (1969), but synonyms include "chemical fossils" (Eglinton and Calvin 1967), "molecular fossils" (Calvin 1969) and "biomarkers" (Seifert and Moldowan 1981), the latter being the most widely-used epithet at present.

Following the pioneering work of Treibs (1934), in which a biogenic origin for crude oils was implied on the basis of the structural similarity between the porphyrin skeleton and chlorophyll *a*, numerous studies have established precursor/product relationships between bio- and geolipids (Erdman 1965; Eglinton and Calvin 1969; Albrecht and Ourisson 1969 ; Maxwell *et al.* 1971; Blumer 1973 and Brassell *et al.* 1980). In immature sediments, the compounds inherit structural features, such as stereochemistry and carbon-number distributions, which result from the enzymatically-controlled biosynthesis of their biological progenitors. With increasing burial, microbially- and thermally-induced modification of the original three-dimensional molecular framework and carbon-number distribution occurs, leading to the retention of the main part of the biomarker skeleton, but resulting in the dilution of the overall biomarker concentration by their own breakdown products. The extent to which the alteration occurs depends on the structure of the biogenic precursor. Relatively inert, structurally simple molecules such as *n*-alkanes are incorporated within the geosphere virtually intact, whilst more complex substances such as acids, ketones and sterols may undergo defunctionalisation, aromatisation, optical and structural isomerisation and ring cleavage. The net result of (mainly) thermal alteration, therefore, is the production of a highly complex molecular mixture comprising various biomarker skeletal structures and other compounds in mature sediments and petroleums.

As sediments pass through the late stage of catagenesis and into the zone of metagenesis, biomarkers become increasingly difficult to detect. This is because their concentrations are decreasing not only relative to other organic species as as result of dilution by the material generated from the thermal breakdown of kerogen, but in absolute terms due to cracking of the biomarker skeletal frameworks themselves (Rullkötter *et al.*1984b;Mackenzie *et al.* 1985).

The last two decades have seen an almost exponential increase in the number of biomarker compounds isolated and identified which has led to a greater appreciation of their structural diversity. Two main factors are responsible for the increase: first, major advances have occurred in analytical techniques over this period, particularly within the field of gas chromatography-mass spectrometry (gc-ms) and associated data-acquisition systems; and second, there is currently a much better understanding of the mechanisms involved in the transformation of organic matter following its deposition. As a result of these developments, the utility of biomarkers as indices of source input, thermal maturation and correlation is now well established, and comprehensive reviews of their occurrence and use have been given in several recent publications (Mackenzie 1984; Philp 1985a,b; Johns 1986; Volkman 1988). A brief synopsis of the geochemical characteristics

of the different biomarker classes investigated in this thesis is given below, with particular reference to their application in geological studies.

2.3.3.1 *N*-Alkanes

N-Alkanes (I) are ubiquitous in geological environments and are also widely distributed in higher plants, algae and other organisms (Douglas and Eglinton 1966). Their structural simplicity has not prevented them from being successfully used as indicators of source input, this application generally being restricted to recent sediments and immature source rocks where the variation in carbon-number distribution is greatest and where *n*-alkane fingerprints can be most confidently matched with those in living organisms.

I

Many recent sediments from a wide variety of environments display long-chain *n*-alkane distributions (n-C_{25}-C_{33}) in which there is a strong odd carbon-number predominance (Stevens *et al.* 1956; Bray and Evans 1961; Kvenvolden 1962). The occurrence of this distribution in both recent and ancient sediments is invariably attributed to a contribution from continental organic matter since the lipid extracts of plants, and particularly those of leaf waxes, have been shown to contain comparable *n*-alkane distributions (Eglinton *et al.* 1962; Eglinton and Hamilton 1963). The overprinting of any inherent non-continental molecular signature by terrestrial material occurs because the latter contains much higher concentrations of *n*-alkanes, the odd carbon-number preference being inherited either directly from the plant or *via* early diagenetic defunctionalisation of even-numbered acids, alcohols or esters (Eglinton and Hamilton 1963). Thus for many recent sediments, irrespective of provenance, it is the continental material which defines the *n*-alkane fingerprint.

A commonly used measure of the predominance of odd over even *n*-alkanes is the Carbon Preference Index (CPI), first formulated by Bray and Evans (1961). It was originally defined over the range of n-C_{25}-C_{33}, but may be applied to any selected interval where the general formula is:-

$$CPI = \frac{1}{2} \frac{(C_z + C_{z+2} \ldots\ldots C_{z+n}) + (C_{z+2} \ldots\ldots\ldots\ldots\ldots C_{z+n+2})}{(C_{z+1} + C_{z+3} \ldots\ldots C_{z+n+1})}$$

Living plant material has CPIs of *c.*10+ whilst values of between 2 and 10 are commonly encountered in recent marine and freshwater sediments (Bray and Evans 1961, 1965).

Although long-chain *n*-alkanes dominate the hydrocarbon fingerprints of higher-plant extracts, high molecular-weight *n*-alkanes (and alkenes) have also been recorded in blue-green algae (Han *et al.* 1968a,b; Gelpi *et al.* 1968,1970) and higher algae (Clark and Blumer 1967; Han *et al.* 1968a,b; Gelpi 1968, 1970; Han and Calvin 1969a; Paoletti *et al.* 1976a), among which odd carbon-numbered homologues are dominant. High molecular-weight *n*-alkanes have also been reported in bacteria, most notably in the non-photosynthetic varieties, although these show no odd-over-even predominance (Davies 1968; Han *et al.* 1968b; Han and Calvin 1969a; Albro and Dittmer 1970; Albro 1976).

Several species of fungi have been found to contain long-chain *n*-alkanes with very high odd carbon-number preferences (Oro *et al.* 1966; Weete 1972, 1976). Possible contributions of organic matter other than that of terrestrial origin should not, therefore, be dismissed when high molecular-weight *n*-alkane distributions are recorded in recent or ancient sediment extracts.

N-Alkane distributions with an even-over-odd carbon-number predominance are not as widespread as those with odd-over-even preferences, although several examples of the former type of distribution have been documented in many recent and ancient sedimentary sequences, mainly in association with evaporitic and anoxic facies, as well as in carbonate-dominated sedimentary regimes. (Welte and Ebhart 1958; Welte and Waples 1973; Debeyser *et al.* 1977; Tissot *et al.* 1977; Guoying *et al.* 1980; ten Haven *et al.* 1985). Even carbon-number preferences have also been reported in a few crude oils (Albaiges and Torradas 1974; Tissot *et al.* 1977; ten Haven *et al.* 1988) and bitumens (Douglas and Grantham 1974).

The diagenetic reduction of fatty acids and alcohols under highly reducing conditions has been proposed to account for even-numbered preferences in recent sediments (Welte and Ebhart 1958; Welte and Waples 1973), whilst Shimoyama and Johns (1972) have invoked the carbonate-catalysed cleavage of two carbon atoms from even-numbered fatty acid precursors, thus explaining the retention of even carbon-numbered straight chains in extracts from many carbonate-bearing successions.

Other workers have proposed that bacterial influences govern the dominance of even-numbered *n*-alkanes, either through the microbial reworking of blue-green algae (Dembicki *et al.* 1976) or from direct bacterial synthesis (Spiro and Aizenshtat 1977; Grimalt *et al.* 1985; Nishimura and Baker 1986).

Although many factors may lead to the predominance of even carbon-numbered *n*-alkanes in sediments, the most widespread operative process is considered to be

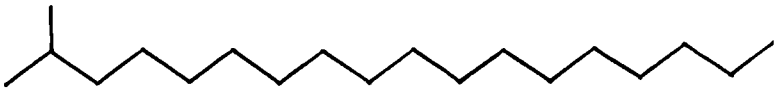
reduction of fatty-acid precursors since even-over-odd preferences are invariably associated with a predominance of phytane over pristane, another ratio widely considered to be indicative of highly reducing conditions (Welte and Waples 1973).

N-Alkane distributions dominated by homologues in the medium molecular-weight range (n-C_{14}-C_{24}) are usually ascribed to bacterial and/or algal input. Any marked odd-over-even predominance is typically defined by enhanced concentrations of n-C_{17} and n-C_{15}. Both of these n-alkanes are prominent in algae; the former is the major component in benthic green and red algae (Clark and Blumer 1967; Han *et al.* 1968b; Han and Calvin 1969a; Youngblood *et al.* 1971), phytoplanktonic algae (Clark and Blumer 1967; Han *et al.* 1968b; Gelpi *et al.* 1968, 1970; Blumer *et al.* 1971; Youngblood *et al.* 1971) and blue-green algae (Han *et al.* 1968b; Weete 1976), whilst n-C_{15} dominates the n-alkane profiles of brown algae (Clark and Blumer 1967; Youngblood and Blumer 1973). Major contributions of n-C_{17} are also found in bacterial n-alkane distributions, although these are not associated with any odd-over-even preference in the medium molecular-weight range (Han and Calvin 1969a; Han 1970).

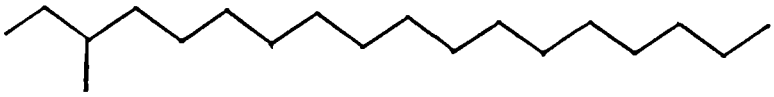
With increasing maturity, the source specificity of n-alkane distributions is lost as new n-alkanes without a carbon-number predominance are generated from kerogen. The net result is the progressive conversion of a distribution in which there was a marked odd-over-even carbon-number predominance into one with no, or little, carbon preference (Brooks and Smith 1969; Albrecht and Ourisson 1971). With further maturation, cracking reactions lead to a shift in the n-alkane maximum towards lower carbon numbers. Most mature sediments and oils consequently show smooth n-alkane distributions in which the CPI values are reduced to c.1. Caution must,however, be exercised when using CPIs as maturity parameters as CPIs of 1 do not necessarily imply maturity. The ratio may vary considerably over relatively short stratigraphic intervals, due to fluctuations in organic-matter type (Huc 1976). Low CPIs can be recorded in immature sediments when there has been a negligible terrestrial contribution and/or where there has been an input of bacterial or algal hydrocarbons with no odd-over-even carbon preference.

2.3.3.2 Branched Alkanes

The most widespread simple-branched molecules are the iso-(2-methyl)(**II**) and anteiso-(3-methyl)(**III**) alkanes reported in many ancient and recent sediments as well as crude oils. They have been isolated from plant waxes (Eglinton and Hamilton 1963) where they occur over a comparable carbon-number range as the n-alkanes and also possess an odd-over-even carbon preference. The presence of this iso- and anteiso alkane fingerprint in geological samples is therefore indicative of a terrigenous input (Arpino 1973).



II

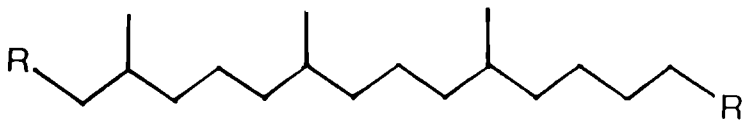


III

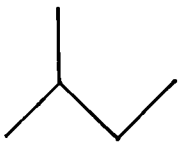
Distributions of iso-and anteiso alkanes spanning a much wider molecular-weight range than those found in higher plants have been detected in many samples and are thought to have originated from bacterial fatty acids (Johns *et al.* 1966 ; Leo and Parker 1966; Kaneda 1967; Cooper and Blumer 1968). High concentrations of these compounds in ancient sediments probably reflect significant microbial reworking of the primary substrate (Tissot *et al.* 1978; Powell 1984).

Other monomethyl alkanes include the 5-, 6-, 7- and 8-methylheptadecanes which occur in relatively large amounts in blue-green algae (Han *et al.* 1968a; Han and Calvin 1970; Gelpi *et al.* 1970). A more obscure series of mid-chain monomethyl alkanes, including the 9-, 10-, 11-, and 12-methyl members, has been described from several Precambrian crude oils where an origin from the bacterial and archaebacterial biomass has been inferred (Makushina *et al.* 1978; Fowler 1984; Klomp 1986; Fowler and Douglas 1987).

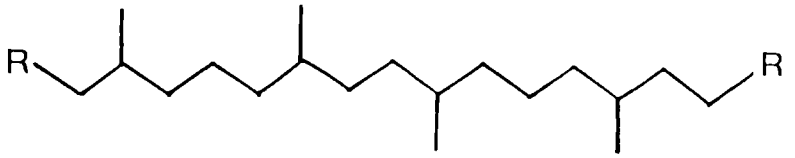
Acyclic isoprenoids are ubiquitous components in sediments and crude oils and are characterised by skeletal frameworks based on the C_5 isoprane unit(**IV**). Three main types of isoprenoid linkage are recognised; the regular "head-to-tail"(**V**) and irregular "head-to-head"(**VI**) and "tail-to-tail"(**VII**) linkages.



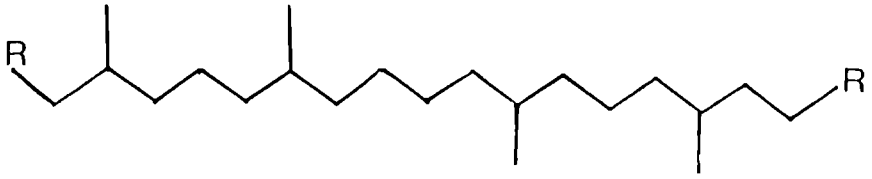
Head - Tail **V**



IV

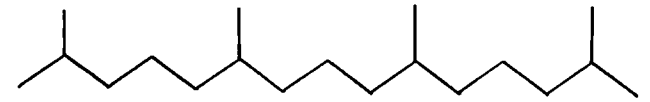


Head - Head **VI**

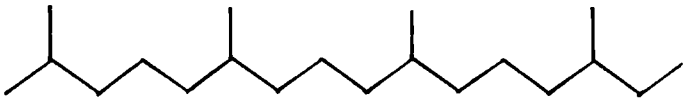


Tail - Tail **VII**

The regular acyclic isoprenoids are the most widespread series in the geosphere, of which the C_{13}-C_{20} members provide the greatest contribution. Regular isoprenoids with chain lengths up to C_{40} (Albaiges *et al.* 1978) and, more rarely, up to C_{45} (Albaiges 1980) have been detected in some petroleums. The branched and cyclic alkane fractions of most rock extracts and oils tend to be dominated by the C_{19} (pristane)(**VIII**) and C_{20} (phytane)(**IX**) components which, along with the other isoprenoids less than C_{20}, are considered to derive mainly from the phytyl side chain of chlorophyll *a* (Bendoraitis 1962). It is this underlying premise on which the utility of the pristane to phytane ratio (Pr/Ph) as an environmental indicator is dependent.



VIII



IX

Brooks *et al.* (1969) originally proposed that Pr/Ph ratios could be used as palaeoenvironmental indicators, based on their observations that high ratios (>1) were invariably associated with oxidising, coal-swamp facies whereas low ratios (<1) were found in more reducing deltaic and marine environments. The underlying rationale was that oxygenated coal-swamp environments promoted the preferential formation of pristane, from phytol, *via* an oxidative pathway involving decarboxylation, whilst phytane was preferentially generated under more reducing conditions by the reduction and dehydrogenation of phytol, thus leaving the C_{20} isoprenoid skeleton intact. Fluctuating oxygen levels in the environment at the time of sediment deposition were therefore deemed to be major controls on the relative amounts of pristane and phytane preserved in geological samples.

This idea was expanded by Powell and McKirdy (1973) who used the Pr/Ph ratios of crude oils as indicators of the depositional environments of their source rocks. High-wax oils generated from non-marine sediments had high Pr/Ph ratios (5-11) in comparison with oils derived from marine source rocks (<1-3). Although broadly correct, these interpretations represent oversimplifications for two main reasons: first, the diagenetic degradation of chlorophyll has since been shown to be far more complex than previously supposed (Didyk *et al.* 1978) and second, the Pr/Ph ratio is a rank-dependent parameter; it increases up to a rank corresponding to $\%R_o \approx 0.7\text{-}1.0$, beyond which the ratio falls sharply (Connan 1974; Albrecht *et al.* 1976; Radke *et al.* 1980). Modification of the Pr/Ph ratio by thermal maturation does not usually proceed to such a degree that the inherent palaeo-

environmental information is completely obscured (Didyk *et al.* 1978; Connan and Cassou 1980).

Recent papers have highlighted the need for caution when utilising the Pr/Ph ratio as an indicator of redox conditions prevailing during sedimentation (Goosens *et al.* 1984; Volkman and Maxwell 1986; ten Haven *et al.* 1987; Volkman 1988), this stemming from the current realisation that the fundamental assumption on which the ratio is based, *viz.* Pr and Ph formation from phytol, is not universally applicable. The importance of archaebacteria as sources of phytane has been increasingly recognised over the past few years, and it now seems that the very low Pr/Ph ratios recorded in many sediments may reflect a major contribution of archaebacterial lipids, particularly those of methanogenic and halophilic bacteria (Holzer *et al.* 1979; Brassell *et al.* 1981; Rissatti *et al.* 1984; ten Haven *et al.* 1988).

Sources other than the diagenetic alteration of chlorophyll-derived phytol have been proposed for pristane. High pristane concentrations observed in some recent sediments have been ascribed to a direct input from zooplankton (Blumer *et al.* 1963; Blumer and Thomas 1965). A derivation from tocopherols has been advanced as an alternative origin for pristane in ancient sediments and petroleums (Goosens *et al.* 1984). It is thus becoming clear that the Pr/Ph ratio may not be as dependent on differences in the pathway of phytol diagenesis as once thought, but nevertheless, the use of the ratio is still justified providing the importance of archaebacterial contributions (and other potential sources of Pr and Ph) can be established from other biomarker evidence (Powell 1988).

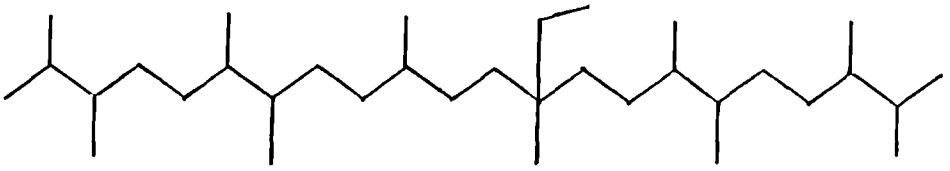
In addition to the Pr/Ph ratio, the Pr/*n*-C_{17} ratio has been introduced as an environmental indicator. Powell and McKirdy (1973, 1975) showed that Australian crudes of terrestrial origin often displayed high Pr/*n*-C_{17} ratios. Lijmbach (1975) also noted a correlation between the Pr/*n*-C_{17} ratios of crude oils and their inferred source-rock depositional environments. Oils deriving from inland peat-swamp environments had ratios greater than 1 whereas those generated from sediments deposited in open-water conditions had ratios less than 0.5. Intermediate ratios of 0.5-1.0 were thought to indicate source rocks deposited in environments with alternating swamp and open-water conditions. No correlation was noted between Ph/*n*-C_{18} and depositional environment. These differences in the isoprenoid/*n*-alkane ratios were attributed to variations in bacterial activity. In open-water environments, bacterially-induced oxidation of phytol is thought to occur, leaving little available for conversion into isoprenoids (Lijmbach 1975). The mechanism has been invoked to explain why many waxy oils generated from open-water, lacustrine sequences are depleted in isoprenoids (Powell 1984).

The ratio Pr/*n*-C_{17} (and Ph/*n*-C_{18}), like that of Pr/Ph, is rank dependent, decreasing significantly with increasing thermal maturation as dilution of the isoprenoids occurs by alkanes generated from kerogen cracking (Tissot *et al.* 1971; Welte *et al.* 1975). Recent work has also shown that variations in this ratio may be related to hydrocarbon expulsion effects (Leythaeuser and Schwarzkopf 1986).

Although subordinate to the regular isoprenoids in terms of widespread occurrence and abundance, irregular isoprenoids have been reported in many sediments and crude oils (Han and Calvin 1969b; Albaiges and Torradas 1977; Michaelis and Albrecht 1979; Chappe *et al.* 1980). These compounds are characterised by "head to head" (Moldowan and Seifert 1979; Albaiges 1980) and "tail to tail" linkages (Brassell *et al.* 1981) and are thought to derive from archaebacterial-membrane lipids. Archaebacteria are considered to be the most primitive forms of life and are restricted to specific ecological niches corresponding to extreme environments. They synthesise a variety of lipids based mainly on the C_{20}, C_{25}, C_{30} and C_{40} acyclic isoprenoid skeletons and are distinguished from "normal" eubacteria in that the isoprenoid structures are attached to glycerol through an ether rather than an ester bond (De Rosa *et al.* 1977; Tornabene *et al.* 1979).

There has been much interest in archaebacterial lipids over the past few years because, as mentioned above, they are now recognised as a major alternative source of phytane in the geosphere, thereby affording an explanation for many of the anomalously low Pr/Ph ratios recorded in some sedimentary sequences.

Perhaps the most source specific acyclic isoprenoid discovered to date is the C_{34} branched alkane botryococcane(X).



X

The only known precursor of this compound is botryococcene which has been isolated from the chlorophycean alga *Botryococcus braunii* (Maxwell *et al.* 1968). Since the extant alga only lives in restricted, fresh-brackish water lacustrine environments, the presence of botryococcane in oils and bitumens is suggestive of derivation from organic matter which accumulated under similar conditions.

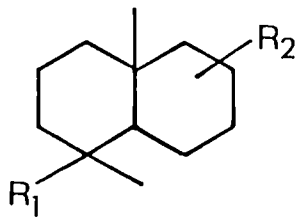
Botryococcance has been identified in some Indonesian oils (Moldowan and Seifert 1980; Seifert and Moldowan 1981), as well as in many Australian oil seeps (McKirdy *et al.* 1986). The presence of botryococcane, in conjunction with other geochemical data, has been used to infer a lacustrine origin for these seeps even though the source rock has not yet been drilled.

Several new botryococcene-related hydrocarbons have been isolated from extant *Botryococcus* colonies (Wake and Hillen 1981; Galbraith *et al.* 1983; Metzger *et al.* 1985), some of which may be precursors to the C_{31} and C_{33} "botryococcanes" recently identified in the lacustrine Maoming shale in China (Brassell *et al.* 1986, 1988).

2.3.3.3 Polycyclic Terpanes

2.3.3.3.1 Bicyclics

Members of a series of C_{14}-C_{16} bicyclic alkanes based on the sequiterpenoid skeleton (**XI**) have been found in many sediments (Anders and Robinson 1971; Alexander *et al.* 1984b; Noble 1986), bitumens (Dimmler *et al.* 1984) and crude oils (Bendoraitis 1974; Kagramanova *et al.* 1976; Vorob'eva *et al.* 1978; Seifert and Moldowan 1979; Philp *et al.* 1981; Richardson and Miller 1982; Alexander *et al.* 1983a,1984b; Noble 1986a; Weston *et al.* 1989). Unsaturated analogues have also been identified in low-rank coals and lignites (Baset *et al.* 1980; Hagemann and Hollerbach 1980).



XI

R_1 = H or CH_3
R_2 = C_2H_5 or C_3H_7

Many theories for the origin of these bicyclic alkanes have been advanced, including derivation from steroidal precursors (Anders and Robinson 1971), pentacyclic triterpenoids (Anders and Robinson 1971; Bendoraitis 1974; Kagramanova *et al.* 1976), tricyclics (Philp *et al.* 1981; Dimmler *et al.* 1984) and tetracyclic alkanes (Rullkötter and Wendisch 1982). The widespread spatial and temporal distribution of bicyclic alkanes in the geosphere, particularly those based on the drimane skeleton, points to an origin from similarly ubiquitous precursors. Prokaryotic micro-organisms, present in a wide range of geological environments, are therefore currently considered to be the most likely progenitors from which the bicyclics derived either through microbial degradation of the pentacyclic hopanoids (Alexander *et al.* 1983a; 1984b). major constituents of micro-organisms, or possibly through direct bacterial synthesis (Noble 1986). Thus, the past use of bicyclic sesquiterpanes as markers for terrestrial input to sediments and oils (Philp *et al.* 1981; Richardson and Miller 1982) may not necessarily be appropriate.

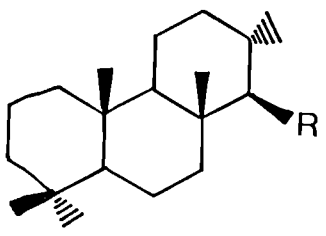
The bicyclic compound eudesmane does, however, appear to be exclusively associated with higher-land plants and, at present, is the only source-specific bicyclic biomarker for this group of organisms (Alexander *et al.* 1983a;1984b).

In addition to the commonly-occurring C_{14} bicyclic alkane, higher molecular-weight bicyclics (up to C_{24}) have been reported in extracts of Green River Shale, for which an origin from steroidal and pentacyclic hopane precursors was inferred (Anders and Robinson 1971). Bicyclics in the C_{15}-C_{24} carbon-number range have also been identified in the Athabasca tar sand bitumen (Dimmler *et al.* 1984) and in many oils from the Taranaki Basin, New Zealand (Weston *et al.* 1989).These are considered to have a microbial origin, either from a C_{25} or C_{30} precursor. Two novel series of bicyclic alkanes in the C_{19}-C_{22} range have recently been discovered in a number of crude oils from China (Zhusheng *et al.* 1988). The marked correlation between the distribution of the bicyclics and that of the steranes has led to the suggestion that the bicyclics are derived from steroidal precursors. This latest work, coupled with the results of previous studies, clearly indicates that bicyclics may derive from various precursors.

Changes in the extent of configurational isomerisation within bicyclics possessing the drimane and homodrimane skeletons have been used as maturation indices, but are restricted in that the equilibrium values are reached well before the onset of the main phase of hydrocarbon generation (Noble *et al.* 1987). Rearranged drimanes may show some potential as maturation parameters as variations in the ratio of rearranged to total drimanes have been observed within a suite of New Zealand oils (Weston *et al.* 1989).

2.3.3.3.2 Tricyclics

Many crude oils and source-rock extracts contain tricyclic terpanes (**XII**) in the C_{19}-C_{45} range. The C_{19}-C_{26} members are generally the most prominent components and are thought to derive from a C_{30} precursor of microbial or algal origin (Aquino Neto *et al.* 1983; Ekweozor and Strausz 1983). The subsequent extension of the tricyclic series up to C_{45} adds further support for a microbial origin, probably from a C_{45} precursor present in bacterial membranes (Moldowan *et al.* 1983).

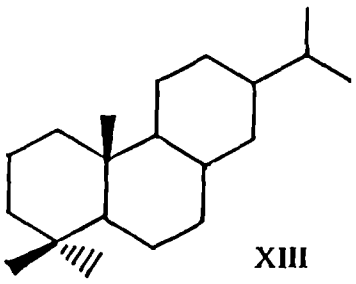


XII

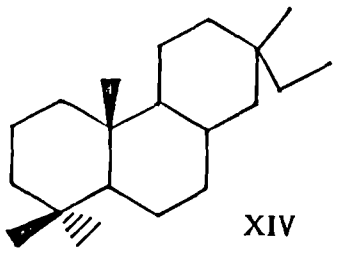
The potential of tricyclic terpanes as palaeoenvironmental indicators has not been thoroughly investigated, although Philp and Gilbert (1986a,b) have commented on the very low concentrations of tricyclics in terrestrially-sourced Australian oils as opposed to the high abundances noted in oils generated from marine sequences. Variations in the distribution and concentration of the individual tricyclics, coupled with their apparent resistance to biodegradation (Reed 1977), is sufficient to assure the value of tricyclic terpanes in correlation studies (Seifert and Moldowan 1979).

Maturity parameters based on tricyclics have recently been introduced, based on changes in the relative amounts of different stereoisomers that occur with increasing maturity (Aquino Neto *et al.* 1983; Chicarelli *et al.* 1988).

Tricyclic diterpanes based mainly on the abietane(**XIII**) and primarane(**XIV**) skeletons have been identified in many recent and ancient sediments (Simoneit 1977; Hagemann and Hollerbach 1980; Snowdon 1980; Barrick and Hedges 1981; Barnes and Barnes 1983; Livesey *et al.* 1984; Venkatesan *et al.* 1986) as well as crude oils (Philp *et al.* 1981, 1983; Richardson and Miller 1982; Snowdon and Powell 1982; Noble *et al.* 1986; Blunt *et al.* 1988) and bitumens (Douglas and Grantham 1974).



XIII



XIV

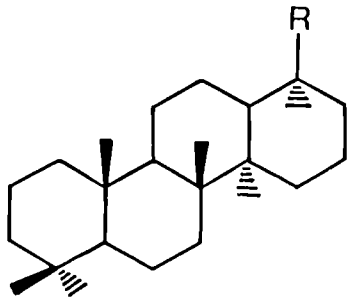
They are thought to derive from corresponding diterpenoid acids which are major constituents of the resins and supportive tissues of higher plants (Thomas 1970). Tricyclic diterpenoids therefore provide excellent markers for a terrigenous contribution to crude oils and sedimentary organic matter.

2.3.3.3.3 Tetracyclics

A series of C_{24}-C_{27} tetracyclic terpanes (17,21-secohopanes)(**XV**) has been detected in many geographically widespread samples of varying ages (Anders and Robinson 1971; Gallegos 1971; Aquino Neto *et al.* 1983). This terpane suite appears to be least abundant, relative to other polycyclic terpanes, in samples from terrigenous facies in which the C_{24} homologue is the most prominent peak

(Aquino Neto *et al* 1983). Philp and Gilbert (1986a,b) have also noticed that the C_{24} component dominates the tetracyclic distribution in many terrestrially-sourced Australian oils and have suggested that this compound may be used as a source indicator.

Three other C_{24} tetracyclic terpanes have recently been recognised in some New Zealand oils and have been tentatively identified as ring A-degraded seco-terpanes (Czochanska *et al.* 1988). Although the precise structures have not yet been established, their presence is thought to corroborate a terrestrial source.

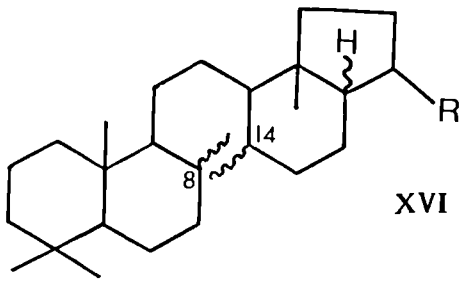


XV

Unsaturated analogues of the 17,21-secohopanes are found in recent sediments (Trendel *et al.* 1982). Their origin has been attributed to the thermocatalytic degradation of hopane precursors, microbial opening of the E ring in hopanoids across the 17,21 bond (see p.83) or the partial cyclisation of squalene. The absence of their saturated tetracyclic counterparts in recent and immature ancient sediments led Trendel *et al.* (1982) to disfavour the last possibility.

Work by Ekweozor *et al.* (1981) suggests that the first hypothesis may be the most appropriate since the distribution of C_{24}-C_{27} tetracyclics in several Nigerian oil fields is best accounted for by thermally-induced rather than by microbially-induced cleavage of the terminal ring of pentacyclic precursors.

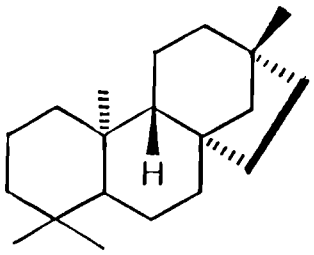
Another series of tetracyclic terpanes thought to originate from pentacyclic hopanoid precursors is the 8,14-secohopanes (Rullkötter and Wendisch 1982; Schmitter *et al.* 1982)(**XVI**).



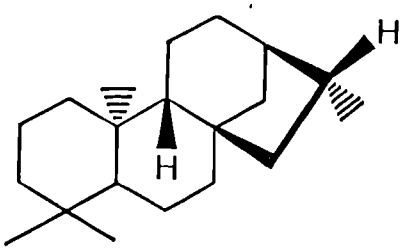
XVI

The distribution of the C_{27}-C_{30}homologues so far discovered parallels that of hopanes in the same samples, suggesting that a relationship exists between them. An origin from pentacyclic hopanoid precursors has been inferred by the C-ring opening, through cleavage of the 8-14 bond, which may be effected by thermal maturation, by contact with the superacid sites of clay minerals (Schmitter *et al.* 1982) or by microbial activity (Rullkötter and Wendisch 1982).

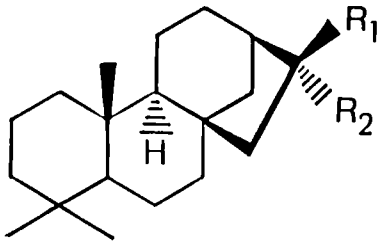
Tetracyclic diterpanes based mainly on the beyerane **(XVII)**, kaurane **(XVIII)** and phyllocladane(**XIX**) skeletons have been documented in the hydrocarbon extracts of a variety of geological materials (Serantoni *et al.* 1978; Hagemann and Hollerbach 1980; Livesey *et al.* 1984; Noble *et al.* 1985a,b, 1986; Alexander *et al.* 1987). Unsaturated tetracyclic diterpenoids have also been identified in recent sediments (Simoneit 1977) and peats (Venkatesan *et al.* 1986).



XVII



XVIII



XIX

The parent compounds of these tetracyclics are thought to be mono-unsaturated alkenes which are particularly abundant in the leaf resins of conifers: indeed the phyllocladenes are restricted to this plant group (Hanson 1968). Akin to the tricyclic diterpanes, the tetracyclic diterpanes provide unambiguous markers for organic matter of terrestrial origin, and in some instances, their source specificity enables them to be related to specific plant families (Aplin *et al.* 1963; Noble *et al.* 1985b).

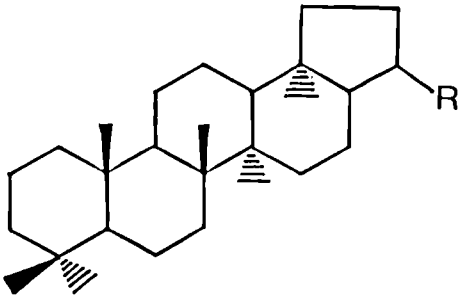
A novel suite of C_{19} tetracyclic diterpanes has been documented in some Russian oils, but structural elucidation is not yet complete (Petrov *et al.* 1988). It is thought that they may have microbial affinities.

Changes in the relative amounts of 16β(H) and 16α(H) epimers in the kauranes and phyllocladanes occur with increasing maturation, and ratios based on these compounds have been used as maturity parameters. As with the bicyclic alkanes, rank determinations based on tetracyclic diterpenoids are restricted to sedimentary successions which have not entered the oil window (Noble *et al.* 1985b; Noble 1986).

2.3.3.3.4 Pentacyclics

Pentacyclic triterpanes of the hopane series are the most extensively used group of 5-ringed biomarkers in petroleum geochemistry. This factor stems from their ubiquity, abundance, structural complexity and high stereospecificity, and has enabled variations in their distributions to provide valuable information on source input, maturity, correlation, biodegradation and migration. They have been documented in sediments and crude oils with a broad range of geological ages and locations, suggesting that the distribution of precursor compounds was similarly widespread (van Dorsselaer *et al.* 1974; Ensminger *et al.* 1974). Hopanes have subsequently been found to be important constituents of prokaryotes, confirming previous suspicions that the origin of hopanes in the geosphere could be attributed to bacterial organisms which are ubiquitous in sedimentary environments (Rohmer and Ourisson 1976a,b; Ourisson *et al.* 1979, 1982).

Members of the regular hopane series commonly occur as C_{27} and C_{29} to C_{35} components and are based on a C_{30} skeletal unit (**XX**). Those with extended side chains in the C_{31}-C_{35} range (Fig.2.7) are thought to arise exclusively from prokaryotic organisms where the precursor is commonly accepted as being the C_{35} tetrahydroxy hopanoid alcohol, bacteriohopanetetrol, which serves as a rigidifier in the cell-wall membranes (Ourisson *et al.* 1979).

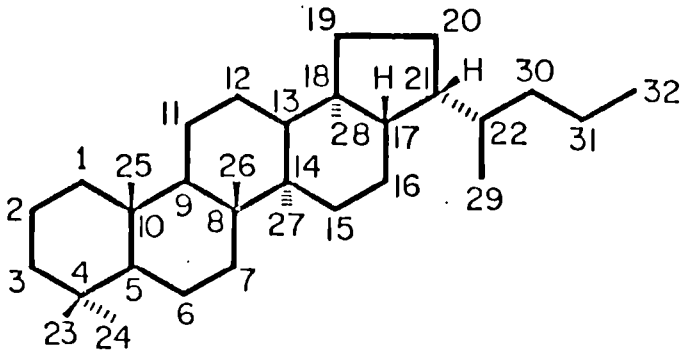


XX

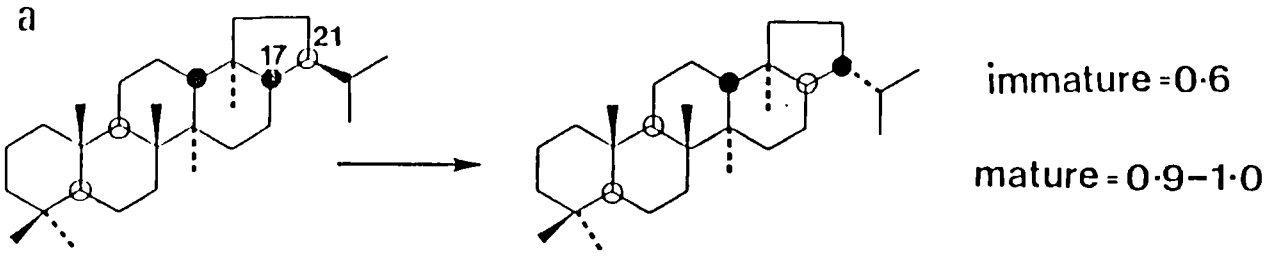
The discovery of hopanes up to C_{40} (Rullkötter and Philp 1981) and C_{70} (Philp 1986) introduces the possibility of even higher molecular-weight progenitors for the hopanes present in fossil fuels.

Hopanes with 30 carbon atoms or less may originate from prokaryotes or eukaryotes. A second major pathway for hopane formation in the former group of organisms is *via* the C_{30} compound diploptene which is also an important constituent of bacterial membrane lipids (Bird *et al.* 1971a; de Rosa *et al.* 1971). This compound has also been found in lower plants such as ferns and mosses (Ourisson *et al.* 1979), Other hopane precursors include pentacyclic triterpenoids with oxygenated functional groups at C-3. These are known from higher plants and give rise to the lupane, friedlane and amyrin triterpane series.

Fig.2.7 Numbering system for the hopane skeleton.



Isomerisation at C-17 and C-21



Isomerisation at C-22

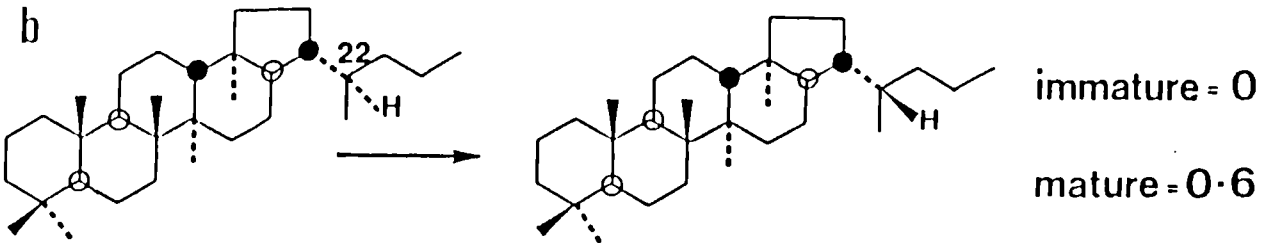
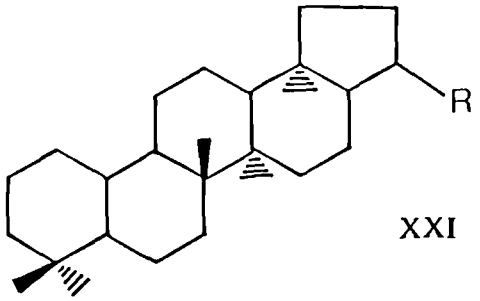


Fig.2.8 Maturation indices based on hopane isomerisation reactions.

The C_{28} member of the regular hopane series is not commonly found in oils and sediments because its formation from higher homologues requires the cleavage of two carbon-carbon bonds in the side chain which is not favourable on kinetic grounds (Kimble *et al.* 1974). It has been observed in high concentrations in some petroleums (Petrov *et al.* 1976; Seifert *et al.* 1978) and sediment extracts (Seifert *et al.* 1978; Bjorøy *et al.* 1980; Grantham *et al.* 1980; Katz and Elrod 1983) where its presence is thought to indicate a restricted depositional environment or may reflect direct input from some as yet unidentified precursor (Grantham *et al.* 1980).

In addition to the regular hopane series, several modified hopane skeletal types have been observed in petroleums and source-rock extracts. Of the C_{27} components, these include the 17α(H), 18α(H), 21β(H)-25,28,30-trisnorhopane which is considered to be the C-10 demethylated analogue of the C_{28} bisnorhopane mentioned above (Volkman *et al.* 1983) and the rearranged 18α(H)-22,29,30-trisnorneohopane (Ts) where the C-28 methyl group is attached to the C-17 rather than to the C-18 position (Whitehead 1974; Pym *et al.* 1975).

Other structural modifications are represented by the nuclear demethylated 25-norhopanes (**XXI**) which have lost the methyl group at C-10.



XXI

Distributions covering the range C_{26}-C_{34} have been found in heavily degraded crude oils (Seifert and Moldowan 1979; Rullkötter and Wendisch 1982; Alexander *et al.* 1983b; Volkman *et al.* 1983b) or in undegraded crudes in which an output from severely degraded hydrocarbons is inferred (Philp *et al.* 1982; Philp 1983; Noble *et al.* 1985).

A series of nuclear-methylated hopanes has been recorded in sediment extracts (Seifert and Moldowan 1978; McEvoy and Giger 1986) which is thought to originate from bacterial hopanoid precursors that are methylated in the A ring. Examples of these compounds have been found in several contemporary bacteria where methylation occurs at the C-3 position (Rohmer and Ourisson 1976c; Zundel and Rohmer 1985) or the C-2 position (Bisseret *et al.* 1985). By synthesising methylhopane standards, Summons and Jahnke (1990) have recently shown that

earlier assignments of the methylhopane series often seen in m/z 205 fragmentograms, and eluting on the trailing side of the analogous hopanes (seen in m/z 191 fragmentograms), are erroneous and are substituted at the C-2(α) position rather than at C-3 as had previously been proposed (Seifert and Moldowan 1978; McEvoy and Giger 1986). Summons and Jahnke (*op.cit.*) also recognised two additional methylhopane series with 2β and 3β nuclear-methyl substitution, the former being confined to immature sediments.

As well as being valuable indicators of source input and biodegradation, hopanes are much used as maturation indices by virtue of the well documented isomeric changes which they undergo with increasing maturation. Hopanes occur in three isomeric series, namely the 17β(H),21β(H) hopanes, 17α(H),21β(H) hopanes and 17β(H),21α(H) hopanes (moretanes), often contracted to ββ, αβ and βα hopanes respectively. The naturally-occurring precursors are nearly always synthesised with the ββ stereochemistry (Ensminger *et al.* 1974; Ourisson *et al.* 1979) although αβ isomers have been recorded in peats (Quirk *et al.* 1980, 1984), lichen and fungi (Corbett and Heng 1977), whilst βα isomers have been found in figs (Galbraith 1965).

The thermal stability of the hopanes increases in the order ββ<βα<αβ and with increasing maturation the ββs isomerises to the more stable forms, but mainly to the most stable αβ configuration (Ensminger *et al.* 1974, 1977) possessed by the majority of hopanes in crude oils and mature sediments. These interconversions form the basis of maturation parameters (e.g. Seifert and Moldowan 1980; Mackenzie *et al.* 1981). A measure of the extent of isomerisation at C-17 and C-21 is given by the hopane/moretane ratio, defined as:-

$$\frac{17\alpha(H),21\beta(H)}{17\alpha(H),21\beta(H) + 17\beta(H),21\alpha(H)} \quad C_{30} \text{ hopanes.}$$

Quoted values in mature sediments and petroleums are generally in the range 0.90-1.00 (90-100%), the end point being reached when no βα hopanes remain (Fig.2.8a; Seifert and Moldowan 1980). Recent work indicates that the aforementioned product-precursor relationship between ββ, βα and αβ hopanes may not be as straightforward as previously supposed since isotopic differences between the above epimers in the Messel Shale indicate that the αβ and βα hopanes are unlikely to have arisen from the epimerisation of ββ hopanes (Freeman *et al.* 1990). The discrepancies in the carbon isotope values are thought to reflect modification of the primary organic matter by bacterial reworking.

For hopanes with more than 31 carbon atoms, additional isomerisation can occur in the C-22 position. Naturally-occurring precursor compounds possess the 22R configuration, but increasing maturation leads to a mixture of 22R and

22S epimers whose equilibrium ratio is *c.*60:40 (van Dorsselaer *et al.* 1975; Ensminger *et al.* 1974, 1977; Seifert and Moldowan 1980). Maturity parameters based on the isomerisation of hopanes at C-22 (Fig.2.8b) are usually calculated using the C_{32} hopanes due to possible coelution of gammacerane with the 22R epimer of the C_{31} homologue. The ratio is defined as:-

$$\frac{22S}{22S + 22R} \quad 17\alpha(H),21\beta(H)\text{-}C_{32} \text{ hopane}$$

The end-point values are *c.*0.55-0.60 which are generally reached before the onset of the main phase of hydrocarbon generation (Seifert and Moldowan 1980; Mackenzie and Maxwell 1981).

Maturation parameters based on C_{27} hopanes are often quoted in organic geochemical studies and are based on the ratio:-

$$\frac{17\alpha(H)\text{-}22,29,30\text{-trisnorhopane (Tm)}}{18\alpha(H)\text{-}22,29,30\text{-trisnorneohopane (Ts)}}$$

This ratio decreases with increasing organic maturation (Seifert and Moldowan 1978) although it does appear to be influenced by variations in organic-matter type (McKirdy *et al.* 1983; Moldowan *et al.* 1986).

Pentacyclic triterpanes other than those of the hopane series have been recorded in sediment extracts and petroleums. They include oleananes and related compounds (Ekweozor *et al.* 1979; Hoffmann *et al.* 1984), lupanes (Rullkötter and Wendisch 1982) and ring A-altered triterpanes (Spyckerelle *et al.* 1977; Corbett *et al.* 1980), all of which are thought to derive from functionalised precursors present in higher plants.

Gammacerane has been observed in many sediments and crude oils (Hills *et al.* 1966; Shi Ji-yang *et al.* 1982; Brassell *et al.* 1983a) and is particularly abundant in hypersaline environments (ten Haven *et al.* 1985, 1988). It has been suggested that gammacerane results from the degradation of tetrahymenol, an important constituent of protozoa (Tsuda *et al.* 1965).

2.3.3.4 Steroidal Hydrocarbons

2.3.3.4.1 Steranes

The stability and distinctive structure of the steroidal skeleton has made it possible to study in great detail the transformations that convert the sterols found in living organisms and recent sediments to the steranes observed in mature sediments and petroleums. The diagenetic fate of sterols is extremely complex and has been reviewed in detail by Mackenzie *et al.* (1982), Brassell *et al.* (1984) and de Leeuw *et al.* (1986). Briefly, the sterol transformations commence in the

water column and continue into the early stages of diagenesis. The sterol precursors, generally possessing Δ^5 double bonds, are defunctionalised and dehydrated to Δ^2 sterenes (*via* stanols) which then isomerise to the more stable Δ^4 and Δ^5 isomers. These sterenes may then be reduced to 5α(H)- and 5β(H)-steranes, but in the presence of clay minerals, reduction competes with acid-catalysed backbone rearrangement, the latter giving rise to diasterenes (Rubinstein *et al.* 1975). Reduction of diasterenes yields mainly 13β(H),17α(H)-diasteranes with smaller amounts of 13α(H),17β(H) components. Further modification of the steroidal skeleton occurs in the later stages of diagenesis and throughout catagenesis enabling steranes to be used as maturation indicators, which is discussed later.

Sterols are widespread in eukaryotic organisms in which they are thought to represent the phylogenetic descendents of hopanoids, acting as membrane reinforcers as hopanes do in the membranes of prokaryotes (Rohmer *et al.* 1979; Ourisson *et al.* 1979). The stereochemical complexity of steroids and their structural diversity, defined by differences in side-chain structure, carbon-number distribution and the presence or absence of a methyl group at C-4, has enabled them to be used as highly sensitive indicators of sources of organic matter in the geosphere (Brassell *et al.* 1980; Brassell and Eglinton 1983).

Sterane distributions in geological samples are usually dominated by C_{27}-C_{29} components. C_{29} sterols are the most abundant sterols in higher plants (Goad and Goodwin 1972) whilst the C_{27} and C_{28} compounds generally dominate sterol distributions in marine organisms (reviewed by Volkman 1986). These assumptions have formed the basis of the construction of triangular diagrams from which the relative amounts of C_{27}, C_{28} and C_{29} steranes have been used to glean information on sources of organic matter and their depositional environments (Huang and Meinschein 1976, 1979). This approach is increasingly being seen as oversimplistic since it is based on only three steranes: the original sterol distribution from which they originated probably possessed a much broader carbon-number range. Of much greater importance is the fact that very few sterols can be considered as unambiguous markers for a specific group of organisms or environment. A recent review (Volkman 1986) has shown that few algal classes can be considered to possess a characteristic sterol distribution, although some sterols are more common in particular algal groups than in others. For example, the C_{28} sterols are the dominant sterols in many diatoms whilst C_{27} sterols are the major components in zooplankton. The occurrence of the C_{29} steranes is rather more capricious. Although sterols are generally absent in prokaryotes, at least in amounts comparable with those

found in eukaryotes, they have, nevertheless, been detected and the distributions are dominated by C_{29} components (De Souza and Nes 1968; Reitz and Hamilton 1968; Paoletti *et al.* 1976b; Boon 1983). The C_{29} sterols are also major contributors to the sterol fractions of green algae (Patterson 1974; Paoletti *et al.* 1976b; Brassell and Eglinton 1983). It is therefore apparent that a high proportion of C_{29} steranes does not necessarily confirm derivation of organic matter from vascular plants. Further vagaries in sterol occurrence are manifested by the fact that several sterols once thought to be restricted to marine milieux have also been recorded in lacustrine environments (Volkman 1986; Wünsche *et al.* 1987). Thus, although plots of C_{27}-C_{29} sterane distributions may prove useful in illustrating the genetic relationships between oils and/or source rocks, inferences about organic-matter source input and depositional environments must be supported by other geochemical, petrological and geological data. The source specificity of steranes may be enhanced through elucidating the structural configuration of the side chain, although this is rarely possible in routine gc-ms analyses.

Three main series of steranes are recognised in sediments and petroleums.

(i) **Regular steranes** (Fig.2.9a). These possess five chiral centres at carbon-numbers 5, 14, 17, 20 and 24, all of which can undergo rearrangement in response to thermal maturation. The steranes initially formed during diagenesis retain the original, biologically-inherited 14α(H),17α(H)-20R configuration which imparts a flat, lath-like molecular shape enabling them to satisfy their function as rigid inserts in cell membranes. This particular configuration is not the most thermodynamically stable structure: hence, with increasing maturation, steranes adopt the more stable 14β(H),17β(H) configuration. The latter, or isosterane, configuration may possess a 5α(H) or 5β(H) stereochemistry, the 5β(H) isomers converting to the more stable 5α(H) form in more mature samples.

The extent of isomerisation at C-14 and C-17 in steranes (Fig.2.10a) is commonly employed as a maturation index and involves the calculation of:-

$$\frac{5\alpha(H),14\beta(H),17\beta(H)}{5\alpha(H),14\beta(H),17\beta(H) + 5\alpha(H),14\alpha(H),17\alpha(H)} \qquad C_{29} \text{ steranes}$$

The end-point value is achieved when the ratio reaches *c.*0.80 (Seifert and Moldowan 1979, 1981; Mackenzie *et al.* 1980a). The ratio of αββ to ααα components is *c.*3:1 in mature samples. The use of this ratio is based on the premise that the transformation of ααα to αββ steranes is a consequence of thermal maturation. Recent detailed re-investigations of the pathways of sterol diagenesis have revealed that αββ steranes may be very early diagenetic products where the precursors are Δ^7 (as opposed to Δ^5) sterols (ten Haven *et al.* 1986; de Leeuw and

Fig.2.9a Numbering system for the regular sterane skeleton.

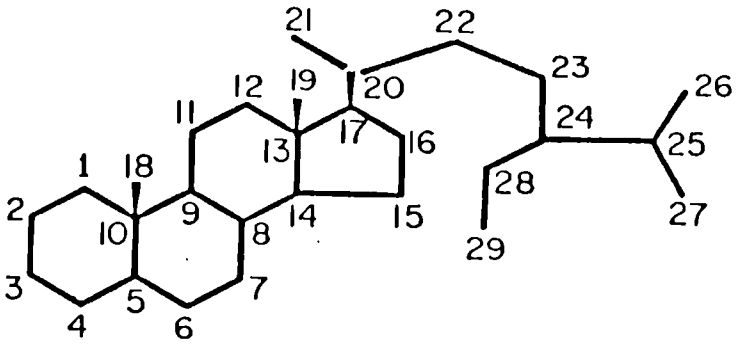
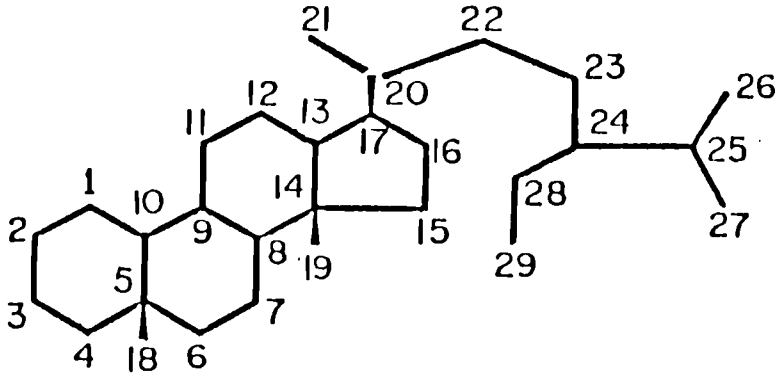
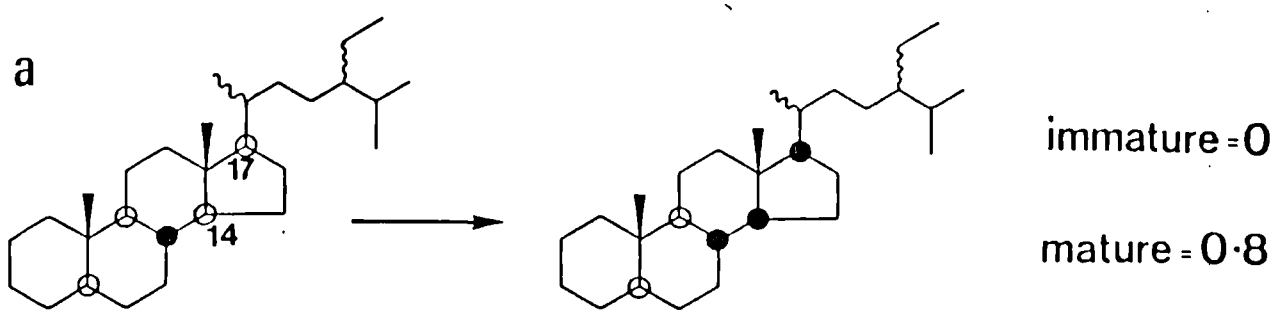


Fig.2.9b Numbering system for the rearranged sterane (diasterane) skeleton.



Isomerisation at C-14 and C-17



Isomerisation at C-20

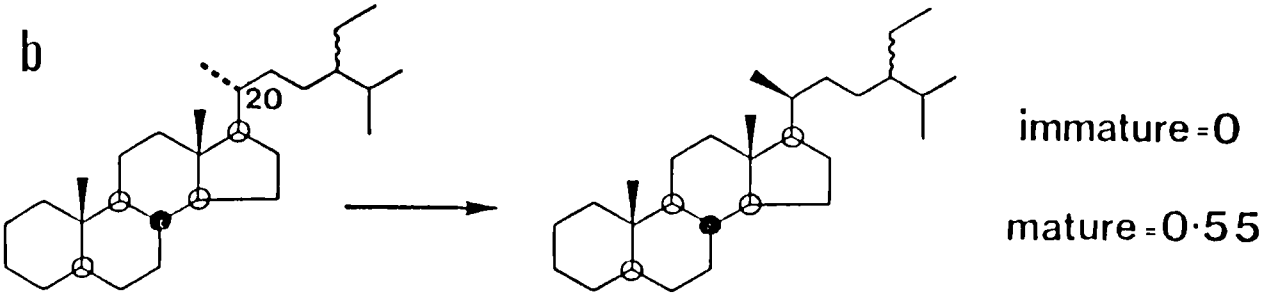


Fig.2.10 Maturation indices based on steranes.

Baas 1986; Peakman and Maxwell 1988; de Leeuw *et al.* 1989). This therefore explains the occurrence of anomalously high maturation indices, based on αββ steranes, in samples from hypersaline environments in which Δ^7 sterols are known to be abundant (Rullkötter *et al.* 1984; ten Haven *et al.* 1985, 1986).

In addition to the stereoisomeric changes at C-14 and C-17, configurational isomerisation also occurs at C-20. Biologically-inherited 20R isomers are converted to an approximately equal mixture of 20R and 20S (Fig.2.10b; Mackenzie *et al.* 1980a). The equilibrium value for the maturation index is *c.*0.55 when calculated according to the following ratio:-

$$\frac{20S}{20S + 20R} \quad 5\alpha(H),14\alpha(H),17\alpha(H) - C_{29} \text{ steranes}$$

This parameter is known to be sensitive to changes in depositional environment (Moldowan *et al.* 1986), matrix effects and heating rates (Mackenzie and McKenzie 1983; Strachan *et al.* 1989).

(ii) **Rearranged steranes** or diasteranes (Fig.2.9b). As mentioned previously, these are thought to derive from diasteranes *via* clay-catalysed reactions under acid conditions (Rubinstein *et al.* 1975). Changes in the stereochemistry at C-13, C-17 and C-20 are the most important within the context of organic geochemical studies. The 13β(H),17α(H) isomers dominate over the 13α(H),17β(H) components with both configurations comprising mixtures of 20R and 20S isomers. In immature sediments these isomers are present in roughly equal proportions (Ensminger *et al.* 1978), but in mature samples the S isomers dominate the distribution in the ratio *c.*60:40 (S:R).

(iii) **4-methyl steranes.** These have been recorded in many sediments and petroleums where they may occasionally be in higher abundance than their 4-desmethyl counterparts, as for example in the Messel Shale (Kimble *et al.* 1979). The major precursor of the 4-methyl steranes is considered to be the 4-methyl sterol dinosterol which, as far as is known, is restricted to dinoflagellates (Boon *et al.* 1979; de Leeuw *et al.* 1983). The occurrence of high concentrations of nuclear-methylated steranes in samples is therefore indicative of dinoflagellate input (Robinson *et al.* 1984). An alternative source of 4-methyl steranes in anoxic environments may be from bacteria, since these compounds have been isolated from the methanogenic bacterium *Methylococcus capsulatus* (Bird *et al.* 1971b), possibly explaining the presence of nuclear-methylated steranes in Precambrian samples, which predate the evolution of dinoflagellates (Fowler and Douglas 1986). The 4-methyl steranes clearly provide a rare example of a class of steranes that are highly source-specific.

2.3.3.4.2. Aromatic Steroids

Aromatic hydrocarbons with more than one condensed aromatic ring are very rare in living organisms, but the inclusion of polyaromatic steroids within the biomarker category is justified on the basis of their undisputed link with biogenic precursor sterols.

Microbially-induced dehydrogenation of sterene precursors is considered to be the major process governing the formation of monoaromatic steroidal hydrocarbons. Compounds aromatised in the A ring (Hussler *et al.* 1981), B ring (Hussler and Albrecht 1983) and the C ring (Seifert and Moldowan 1978) are known in the geosphere. The C-ring monoaromatics are the predominant monoaromatic species in sediments and petroleums.

The production of di- and triaromatised aromatics is considered to be a thermally-driven process commencing mainly from the C ring (II, III, IV in Fig.2.11). Studies of the conversion of C-ring monoaromatics to ABC-ring triaromatics have established that the dominant process involves the loss of a methyl group at C-10 (Mackenzie *et al.* 1981). The C_{27}-C_{29} carbon-number distribution of monoaromatic steroids therefore gives way to one of C_{26}-C_{28} triaromatics. Another series of triaromatic steroids often encountered in sediments and petroleums is characterised by the presence of a methyl group in the A ring at the C-1 and C-4 positions (structures VI and VII in Fig.2.11). These compounds may arise either through the aromatisation of C-ring monoaromatics, followed by a transfer of the C-19 methyl group to the C-1 and C-4 positions, and/or by aromatisation of A-ring monoaromatics already possessing methyl groups at C-1 and C-4 (Ludwig *et al.* 1981). These nuclear-methylated aromatics are not well documented in the literature and consequently their validity as maturation indicators is not known.

All the foregoing monoaromatic hydrocarbons belong to the regular monoaromatic series, Recently, a suite of rearranged monoaromatic hydrocarbons has been identified which is characterised by the shift of the methyl group at C-10 to the C-5 position (Riolo and Albrecht 1985; Moldowan and Fago 1986). The response of these "dia-monoaromatic" steroids to type influences and maturation parallels that of the diasteranes, suggesting a similar mode of formation, *i.e.* acid-catalysed rearrangement.

Regular C-ring monoaromatic steroids possess resolvable chiral centres at C-5 and C-20, giving rise to four possible stereoisomers per carbon number. In mature samples, the 5α(H) form disappears in favour of the more thermodynamically stable 5β(H) isomer. Triaromatic steroids possess only one chiral cantre at C-20, giving rise to two peaks per carbon number. The conversion of mono- to

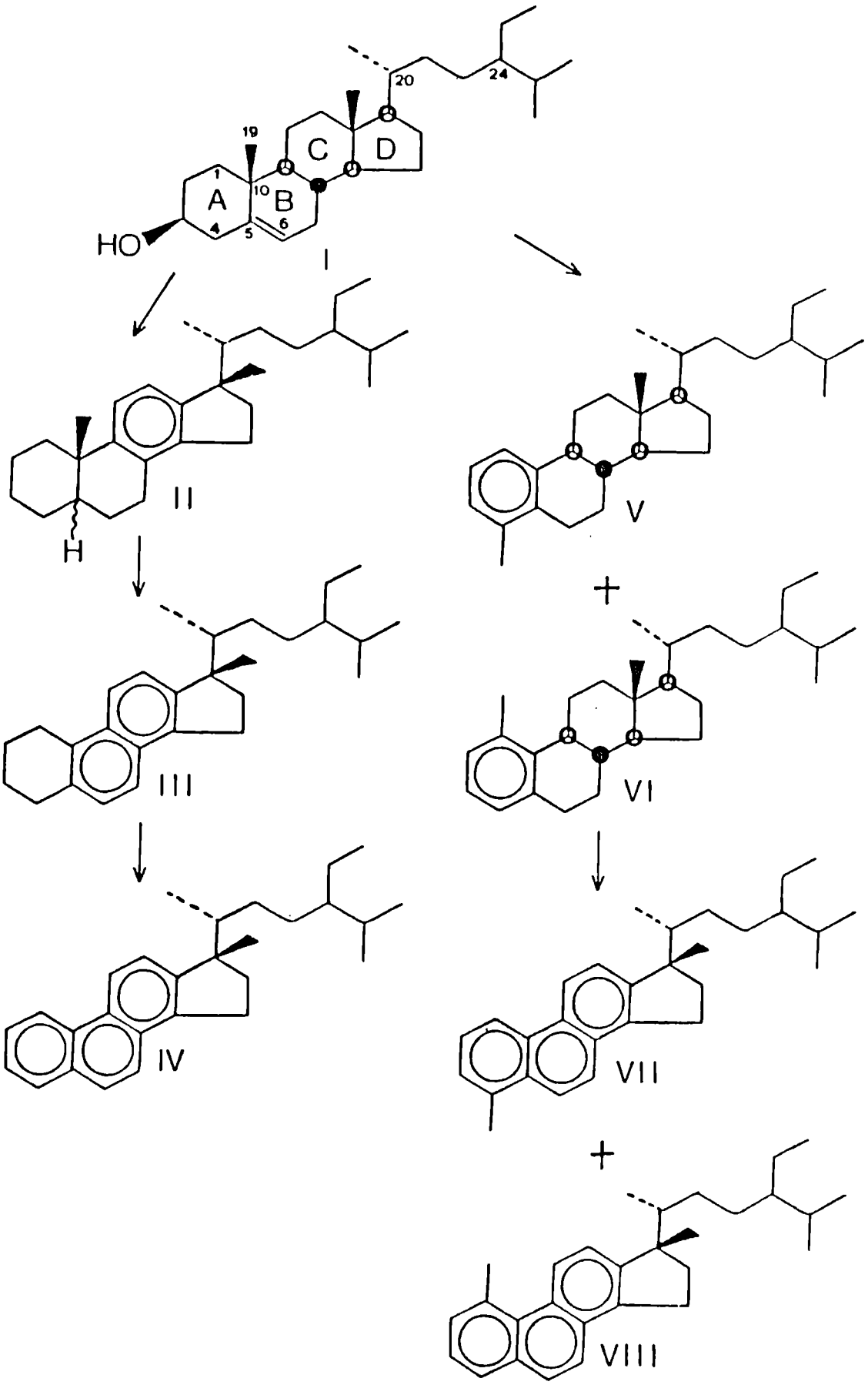


Fig.2.11 Simplified reaction scheme showing the conversion of a sterol to various aromatic hydrocarbons (modified from Mackenzie 1984).

triaromatic steroids is used as a maturation parameter, the measurement of which is given by:-

$$\frac{C_{28}\text{-20R triaromatic}}{C_{28}\text{-20R triaromatic} + C_{29}\text{-20R monoaromatic}} \quad \text{steranes}$$

The resulting value extends from 0 to 1 with increasing maturity over a range similar to that covered by the isomerisation at C-20 in steranes (Mackenzie *et al.* 1981).

Another maturity parameter involving aromatic steroids is based on the thermally-induced enrichment of lower molecular-weight aromatics (C_{20}-C_{22}) which occurs as rank increases (Mackenzie *et al.* 1981). Parameters based on measuring the relative amounts of C_{20} and C_{28} triaromatics are most commonly employed and are derived from the formula:-

$$\frac{C_{20}}{C_{20} + C_{28}} \quad \text{triaromatic steroids}$$

Low molecular-weight monoaromatics and methyl triaromatics also show an increased abundance relative to the high molecular-weight components (Seifert and Moldowan 1978; Mackenzie *et al.* 1981; Shi Ji-yang *et al.* 1982; Wardroper *et al.* 1983; Riolo *et al.* 1986), but ratios based on these series are not commonly reported in the literature. Laboratory experiments have recently shown that the enrichment in low molecular-weight triaromatics with increasing maturation is more likely to be due to the preferential degradation of the components with longer side chains rather than the conversion of one group to another by carbon-carbon bond scission in the side chain (Beach *et al.* 1989). A similar mechanism may account for the relative increase in short-chain components in the other aromatic series.

The various molecular-maturation indices discussed above are applicable over different parts of the rank range as summarised in Fig.2.12, based on the analysis of Mesozoic sample suites from the Paris Basin and NW Germany (Mackenzie and Maxwell 1981).

The diagram must be considered as an approximation since the relative rates of reaction will vary in response to differences in thermal history.

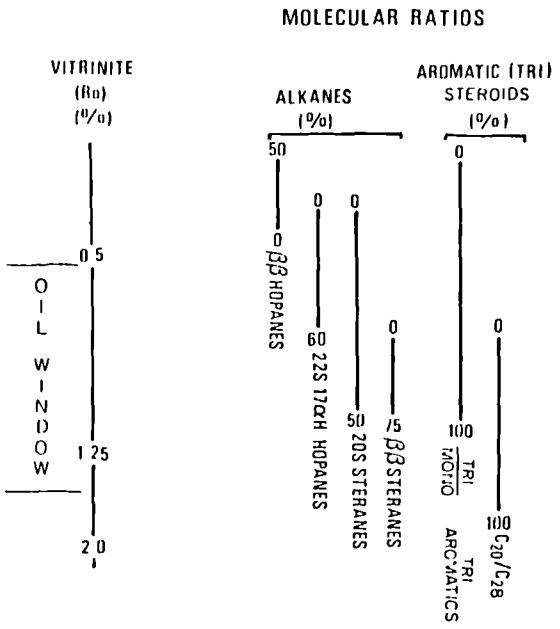


Fig.2.12 Ranges of some molecular maturation parameters plotted against vitrinite reflectance (modified from Murchison 1987, after Mackenzie and Maxwell 1981).

2.3.4 Aromatic Hydrocarbons

Much of the past research on hydrocarbons in organic geochemistry has concentrated on aliphatic compounds, principally because of their relative ease of analysis. By comparison, the study of aromatics has been neglected,but interest has increased dramatically over the past few years, mainly as a result of improvements in analytical techniques and also in response to increasing concern about the toxicity of many of these compounds.

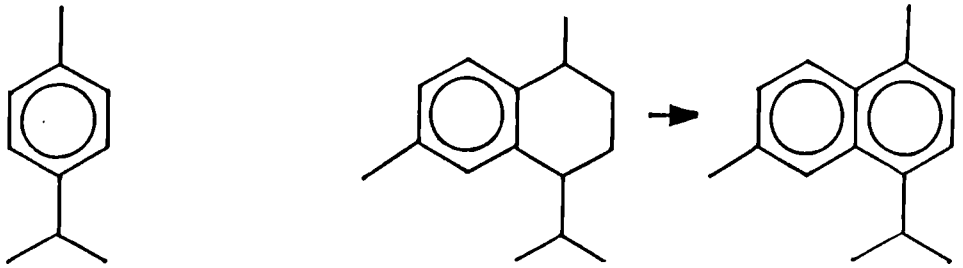
Complex mixtures of aromatic hydrocarbons, particularly those of polycyclic aromatic hydrocarbons (PAH), are virtually ubiquitous constituents of recent sediments, making it necessary to include them as part of the natural background level of hydrocarbons present in aquatic environments (Youngblood and Blumer 1975; Laflamme and Hites 1978). Highly complex aromatic assemblages have also been recorded in a variety of ancient sedimentary materials and petroleums (Mair 1964; Speers and Whitehead 1969; Tissot *et al.* 1971; Youngblood and Blumer 1975; White and Lee 1980; Chaffee and Johns 1983; Mackenzie *et al.* 1983; Killops and Readman 1985).

Despite their complexity and widespread distribution, aromatic hydrocarbons can be classified into two main categories depending on their mode of origin as discussed below.

2.3.4.1 Biogenic and Diagenetic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons are not thought to be synthesised by living organisms, at least in any significant quantities, although much controversy currently surrounds this issue (Grimmer and Düvel 1970; Hase and Hites 1976).

Monoaromatic compounds, however, are known from many higher plants and include compounds such as *p*-cymene (**XXII**) and calamenene (**XXIII**) (Simonsen and Barton 1961; Weiss and Edwards 1980). Further aromatisation of calamenene gives rise to cadalene (**XXIV**) which has been found in many resins and ambers (Simoneit *et al.* 1986; Grimalt *et al.* 1988) as well as in coals (Baset *et al.* 1980; Simoneit *et al.* 1986). The presence of cadalene in recent sediments and aerosols has therefore been taken to be indicative of terrestrial input (Simoneit and Mazurek 1982; Albaiges *et al.* 1984), an origin which also seems feasible for the cadalene reported in a crude oil (Bendoraitis 1974).



XXII **XXIII** **XXIV**

Various mono-, di- and triaromatised tricyclic triterpenoids have been reported in many recent marine (Simoneit 1977; Simoneit and Mazurek 1982), lacustrine (Wakeham *et al.* 1980a,b; Tan and Heit 1981; Barnes and Barnes 1983) and deltaic sediments (Albaiges *et al.* 1984). They are also prominent constituents of resinous plant detritus, woods and ambers (Simoneit *et al.* 1986; Grimalt *et al.* 1988). These aromatic compounds are based mainly on the abietane and primarane skeletal structures which are major constituents of higher plant resins, especially those of conifers (Langenheim 1969; Stonecipher and Turner 1970). Inferred diagenetic pathways for these plant-derived tricyclic aromatic terpenoids are shown in Fig.2.13. It should be noted that retene and pimanthrene may not be unequivocally assigned to abietic and pimaric acid precursors since many other resin constituents are also of the abietane-pimarane skeletal types (Thomas 1969). Additional complications include the possible rearrangement of pimarane to abietane under certain diagenetic conditions, for example, acid catalysis (Schuller and Conrad 1966) and a potential contribution of retene derived from coniferous-wood combustion (Ramdahl 1983).

Other major sources of biogenically-derived PAH are believed to be the progressive aromatisation of higher-plant derived triterpenoid precursors which are oxygenated at the C-3 position (Greiner *et al.* 1976, 1977; Laflamme and Hites 1979; Wakeham *et al.* 1980a,b). Aromatisation of the pentacyclic triterpenes starts in the A ring and proceeds through the D and E rings, accompanied by loss

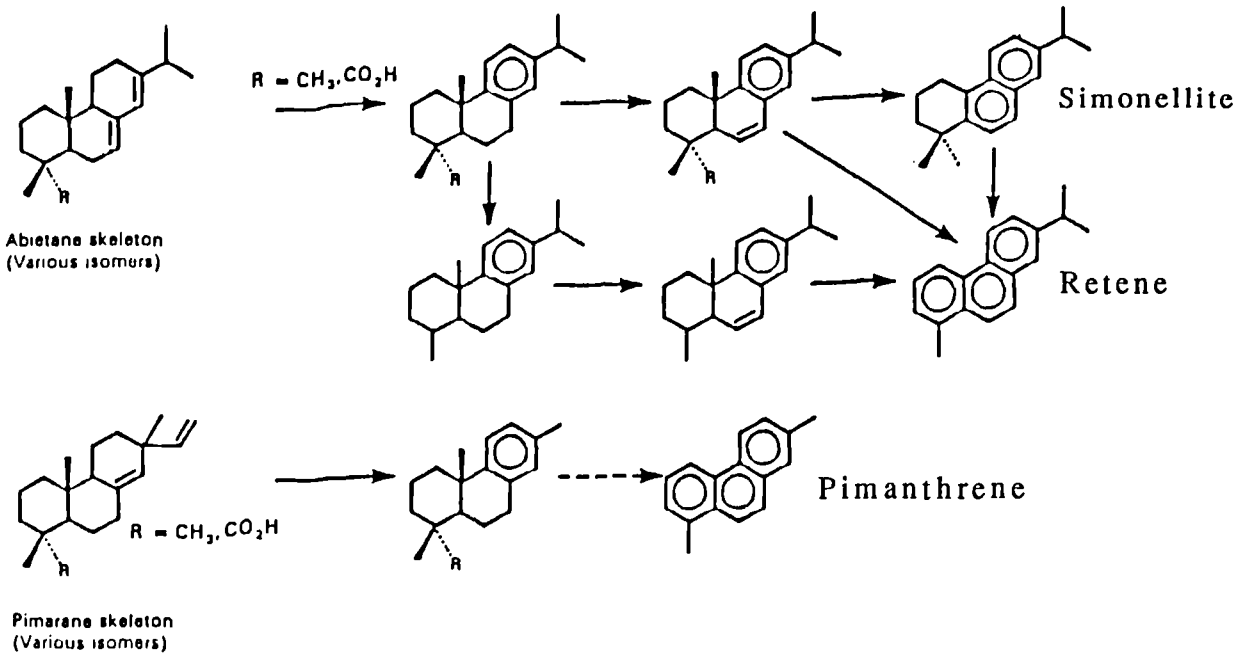


Fig. 2.13 Inferred diagenetic pathways for tricyclic aromatic compounds (modified from Simoneit and Mazurek 1982).

of angular methyl groups. The end products of this reaction route are methylpicenes (XXI and XXII in Fig.2.14) which have been identified in lignites (Streibl and Herout 1969), recent and ancient sediments (Carruthers and Watkins 1964; Greiner *et al.* 1976, 1977; Spyckerelle *et al.* 1977a,b; Laflamme and Hites 1978; Wakeham *et al.* 1980a,b). If the reaction sequence is initiated by cleavage of the A ring, aromatisation commences in the B ring resulting in the formation of methylchrysenes (XXVII and XXVIII in Fig.2.14).

The presence of these PAH in recent sediments, some of which are only a few decades old, clearly points to the importance of micro-organisms in the diagenetic alteration of biogenic precursors to PAH within the sedimentary column (Spyckerelle *et al.* 1977a,b).

Several series of PAH, based on other triterpenoid skeletons, have been documented in coals and sediments (Chaffee and Johns 1983; Chaffee *et al.* 1984; Garrigues *et al.* 1986; Chaffee and Fookes 1988). Most of these compounds can be diagenetically related to the lupane, oleanane and ursane skeletons. Microbially-mediated aromatisation is again thought to be important in the formation of these compounds as they have been recorded in brown coals (Chaffee 1986). A number of structures possessing the 8,14-seco configuration have been identified, where photochemical and acid-catalysed processes have been invoked to explain the C-ring cleavage (Chaffee *et al.* 1984; Chaffee and Fookes 1988).

An additional source of aromatic hydrocarbons in the geosphere is from the transformation of bacterial hopanoid precursors. Such compounds are represented

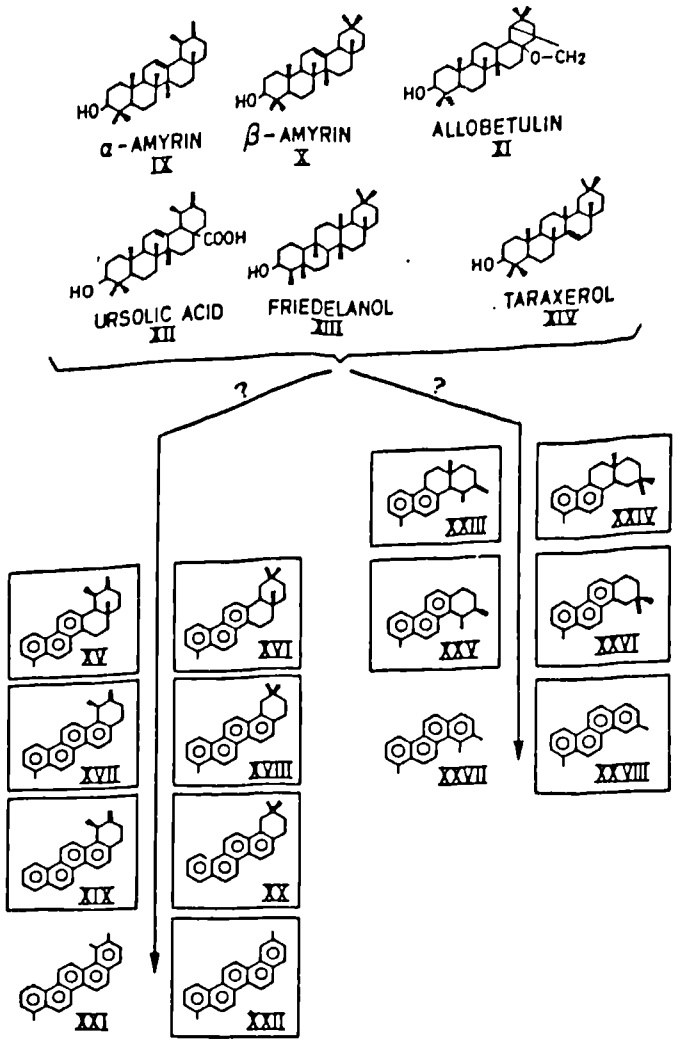
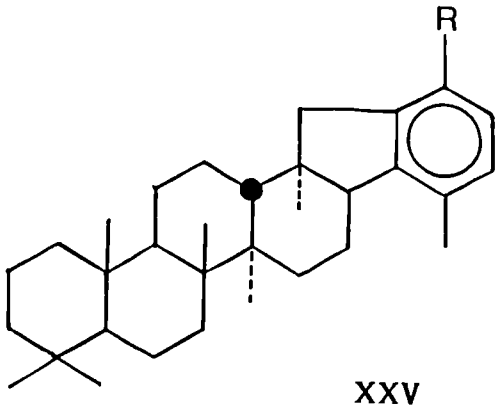


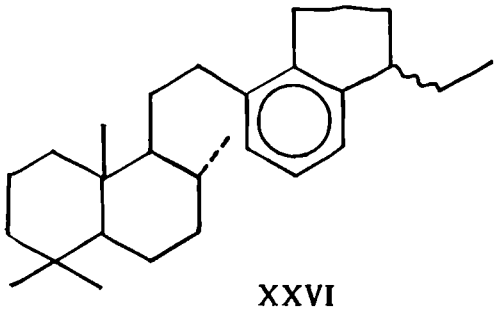
Fig.2.14 Inferred diagenetic pathways for PAH formation from plant-derived pentacyclic triterpenes (from Wakeham *et al.* 1980b).

by the benzohopanes (**XXV**), which have been reported in numerous sediments and petroleums (Hussler *et al.* 1984; McEvoy and Giger 1986). Rearrangement of the inferred bacteriohopanetetrol precursor and its subsequent aromatisation is thought to take place at a relatively early stage of maturation since benzohopanes have been observed in very immature sediments (Hussler *et al.* 1981). Although this compound group has been noted in a variety of sample types, the benzohopanes are particularly abundant in carbonate facies (Hussler *et al.* 1984).

Hussler *et al.* (1984) have also reported a series of D ring monoaromatised 8,14-secohopanes (**XXVI**) and related structures which are abundant in carbonate samples, but comprise only minor constituents of terrestrial and immature samples. These authors have suggested that secohopanes form from hopanoid precursors by the thermocatalytic cleavage of the relatively weak 8,14 bond.

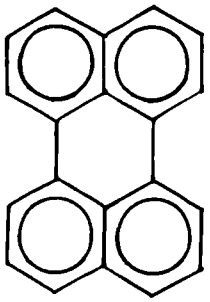


XXV



XXVI

Perhaps the most enigmatic polyaromatic hydrocarbon for which a diagenetic origin has been postulated is perylene (**XXVII**). This compound has been found in many marine and lacustrine sediments where it often dominates the aromatic hydrocarbon distribution (Orr and Grady 1967; Brown *et al.* 1972; Laflamme and Hites 1978; Wakeham *et al.* 1979, 1980b).



XXVII

An early concensus envisaged *perylene formation occurring by the trans*formation of structurally similar erythroaphin and quinone pigments in reducing environments (Orr and Grady 1969; Aizenshtat 1973). These substances have been reported in moulds (Lousberg *et al.* 1969), insects (Cameron *et al.* 1964) and fungi (Thomson 1971), implying a land-derived origin for perylene, but these sources were not thought to be sufficiently abundant to account for the observed levels of perylene in sediments (Watts *et al.* 1977). Furthermore, recent findings of high concentrations of perylene in sediments thought to be largely free of terrigenous input led Wakeham *et al.* (1979) to question the validity of a terrestrial origin. In addition, Hites *et al.* (1980) found high perylene concentrations in a diatomaceous ooze from which they inferred phytoplanktonic precursors.

From a synthesis of much of the currently available data, Louda and Baker (1984) have shown that perylene precursors appear to be present in marine, lacustrine and terrestrial detritus, and that perylene abundance in most environments represents a marker for the development of early depositional anoxia rather than an indication of input from a specific biogenic precursor. In some

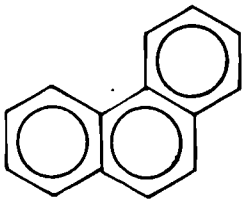
marine sediments, however, perylene could derive from the activities of micro-aerophilic marine benthic microbes.

From the foregoing account, it is apparent that a biogenic origin for PAH can be inferred when their structures can be directly related to the skeletal frameworks of presumed biogenic precursors, making chemically- or microbially-induced aromatisation of naturally-occurring cyclic compounds one possible source of PAH in geological environments. This situation generally leads to the observation of one or two specific compounds in aromatic sediment extracts rather than a complex mixture of PAH and their alkyl homologues. Given the compositional complexity generally observed in aromatic distributions, *in situ* aromatisation is not considered to be a major source of PAH on a global scale.

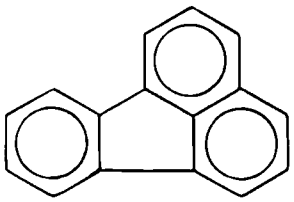
2.3.4.2 Combustion-Derived Aromatic Hydrocarbons

Aromatic hydrocarbon assemblages in soils and recent sediments are extremely complex, but are, nevertheless, far simpler in overall composition than those found in ancient sediments and petroleums. The aromatic compounds found in recent sediments are characterised by a dominance of unsubstituted (parent) polyaromatic hydrocarbons (PAH) and display a remarkable similarity in composition over a wide range of depositional environments (Blumer and Youngblood 1975; Youngblood and Blumer 1975). This virtually ubiquitous compositional consistency has led these authors to suggest that the most recent sediment samples owe their PAH assemblages predominantly to a single mode of origin. The prominence of parent PAH and the relatively low abundance of unstable linear ring systems, also a notable feature of sedimentary PAH, are characteristic features of aromatic mixtures derived from the high- to medium-temperature combustion of organic matter (National Academy of Sciences 1972). The resemblance between the molecular weight distributions of PAH in recent sediments and those of the products of wood combustion led Blumer and Youngblood (1975) and Youngblood and Blumer (1975) to conclude that the source of sedimentary PAH was the burning of plant material in prairie and forest fires. While natural burning may account for a very low background level of PAH in recent sediments, it is not thought to constitute a major source of these compounds since it cannot account for the pronounced increase in PAH concentrations that has been recorded in numerous marine and lacustrine sequences dating from the time of the Industrial Revolution (Grimmer and Böhnke 1975, 1977; Hites *et al.* 1977, 1980; Wakeham *et al.* 1980c; Tan and Heit 1981). The marked increase in PAH abundance, which occurs moving towards the surface sediments in these sequences, correlates

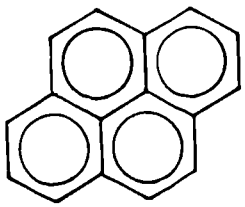
well with the increased anthropogenic combustion of fossil fuels due to industrialisation and vehicular emissions. Higher concentrations of PAH have also been detected with increasing proximity to urban centres (Laflamme and Hites 1978; Gschwend and Hites 1981) and they have also been found to be the dominant constituents of urban air particulates (Lao *et al.* 1973; Lee *et al.* 1976, 1977) in which the major compounds include phenanthrene (**XXVIII**), fluoranthene (**XXXIX**), pyrene (**XXX**), chrysene (**XXXI**) and benzopyrenes (**XXXII**). Both these observations provide further strong evidence supporting an anthropogenic origin for these compounds.



XXVIII



XXIX



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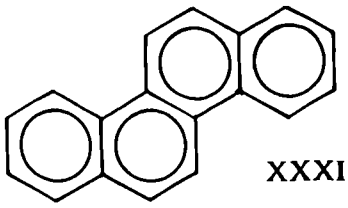
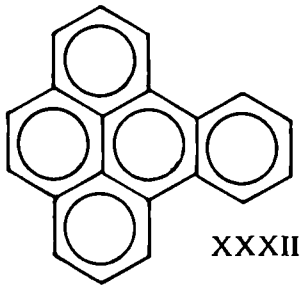
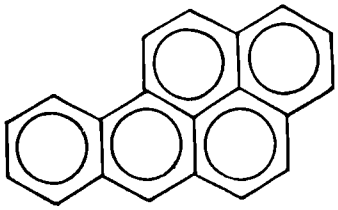


XXXI



XXXII



Notwithstanding the predominantly anthropogenic combustion source for sedimentary PAH, there is a group of naturally-occurring PAH compounds which is thought to derive from the natural combustion/pyrolysis of organic matter. This compound group is represented by the rare hydrocarbon minerals pendletonite, curtisite and idrialite (Blumer 1975). Pendletonite is virtually pure coronene (Murdoch and Geissman 1967) whilst curtisite and idrialite are complex mixtures of various highly condensed, isomeric PAH and their alkyl-substituted homologues (Blumer 1975; Wise *et al.* 1986). These minerals are found within hydrothermal vent systems where they are thought to have formed by the medium-temperature pyrolysis of organic matter followed by prolonged exposure to elevated temperatures in the subsurface. Fractionation and subsequent crystallisation are thought to have occurred during migration from the vent site.

The precise mechanism(s) of PAH formation from the combustion of organic matter is far from being completely understood, but is thought to involve two main reaction pathways *viz.* pyrolysis and pyrosynthesis. Most of the hypotheses in this area derive ultimately from the work of Badger *et al.* (1958) who found

that, at high temperatures, organic compounds are cracked to smaller, unstable molecules (the pyrolysis step) which then recombine to yield larger, more stable aromatic hydrocarbons (pyrosynthesis).

2.3.4.3 Alkylated *versus* Non-Alkylated PAH

PAH assemblages are generally present as complex mixtures of both alkylated and non-alkylated (parent) species. Qualitatively similar PAH mixtures are produced almost regardless of the fuel type and combustion conditions (Hase *et al.* 1976). Quantitatively however, the yields and distribution of parent PAH and alkylated homologues vary markedly depending on such variables as starting material, flame-zone temperature, fuel-to-air ratio and residence time in the hot zone. Very high temperatures (e.g. *c.*1900°C in a carbon black furnace) will yield soot devoid of alkyl PAH while lower temperatures (e.g. *c.*880°C in a cigarette) give aromatic distributions containing abundant alkylated PAH (Lee and Hites 1976; Lee *et al.* 1976b). Prolonged exposure (millions of years) of organic matter to relatively low temperatures (*c.*200°C and below), such as those generally encountered in sedimentary basins, leads to the formation of exceedingly complex and highly alkylated PAH assemblages typified by those in petroleums (Mair 1964) and ancient sediments (Youngblood and Blumer 1975). It is therefore clear that lower formation temperatures preserve a greater degree of alkylation: thus, the relative amounts of alkylated and non-alkylated PAH can give information on the source of these compounds, assuming that there has been no subsequent modification of the distribution e.g. by the preferential solution of alkylated species (McAuliffe 1969).

The nature of the starting material is also important: coal combustion yields far higher quantities of PAH than the burning of oil and gas (National Academy of Sciences 1972; Hites *et al.* 1977) and, furthermore, the PAH distribution is more enriched in alkyl-substituted components (Lee *et al.* 1977; Laflamme and Hites 1978).

2.3.4.4 Aromatic Hydrocarbons as Maturation Indices

Numerous maturation indices based on aromatic hydrocarbons have been developed over the past few years, many of which rely on changes in the configuration of isomers with α-substituted alkyl groups to those possessing thermodynamically more stable β-substituents. The various maturity parameters have recently been reviewed by Radke (1987), but only those used in this project are discussed below.

The most widely-used maturity parameter based on aromatic hydrocarbons is the methylphenanthrene index (MPI) developed by Radke *et al.* (1982a,b). This index measures the extent of rearrangement in the distribution of methylphenanthrene isomers that occurs in response to increasing steric stress brought about by thermal maturation.

Phenanthrenes are thought to originate from steroid and triterpenoid precursors present in biological materials (Mair 1964; Greiner *et al.* 1976). Partial dealkylation of these precursor molecules would yield only 1-and 2-methylphenanthrenes, and so the presence of 3-and 9-methylphenanthrenes as major components in sediments and crude oils has been attributed to the methylation of phenanthrene and the rearrangement of the monomethyl phenanthrenes (Radke *et al.* 1982a). Increasing sample maturity yields larger relative amounts of 2-and 3-methylphenanthrene with respect to 1-and 9-methylphenanthrene and can be explained in terms of the rearrangement of methyl groups in α positions (i.e. 9- and 1-methylphenanthrenes) to the more thermodynamically stable β positions (3- and 2-methylphenanthrenes). These configurations, along with the formula for the most widely-quoted form of the methylphenanthrene index (MPI-1), are shown in Fig.2.15, where P and MP refer to phenanthrene and methylphenanthrene respectively.

The application of the MPI in petroleum geochemistry stems from its strong positive correlation with vitrinite reflectance in the range $\%R_o$ =0.6-1.3 (Fig.2.16). The reversal in trend at the floor of the oil window is thought to reflect the dominance of demethylation reactions. The equations shown in Fig.2.16 can be used to calculate vitrinite reflectance (R_c) from MPI over the appropriate rank range. Correlation of MPI with vitrinite reflectance beyond the oil-death line is only marginal, enabling only an approximate maturity estimate to be made in samples with $\%R_o$ >1.35. From Fig.2.16 it is apparent that the MPI value alone cannot distinguish immature from overmature rocks since these will be fairly similar. The MPI should therefore be used in conjunction with other indices such as the methylphenanthrene ratio (MPR) (Fig.2.17). Unlike the MPI, the MPR does not show a reversal at the base of the oil window, and values greater than c.2.2 are indicative of maturities >$\%R_o$ =1.35 (Radke *et al.* 1984). Use of the MPR will therefore allow the choice of equation in Fig.2.16 from which R_c can be calculated from MPI.

The MPI has been particularly successful in evaluating the maturity of sediments, for example marls and carbonates, which have very low organic contents and which are deficient in primary vitrinite (Radke and Welte 1983). MPI values for oils have proved useful in that they allow an estimation of the

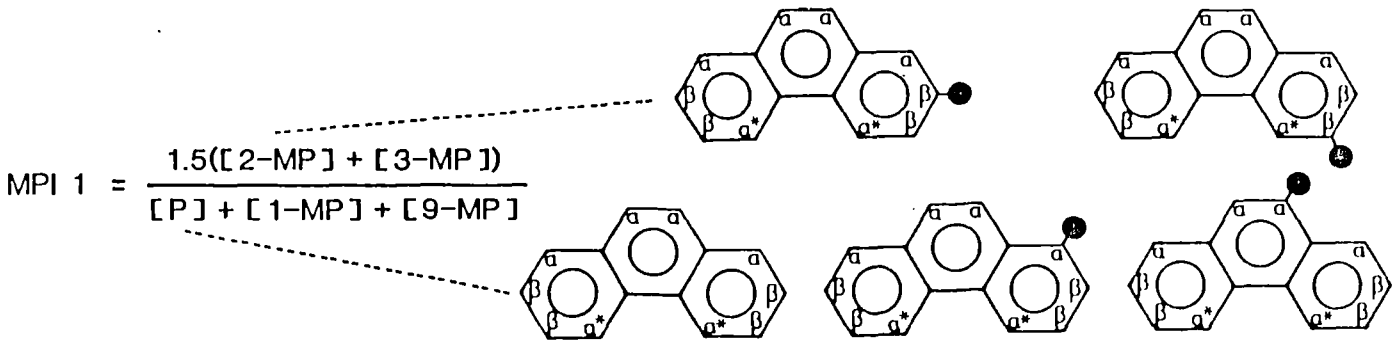


Fig.2.15 The methylphenanthrene index: structures and formula.

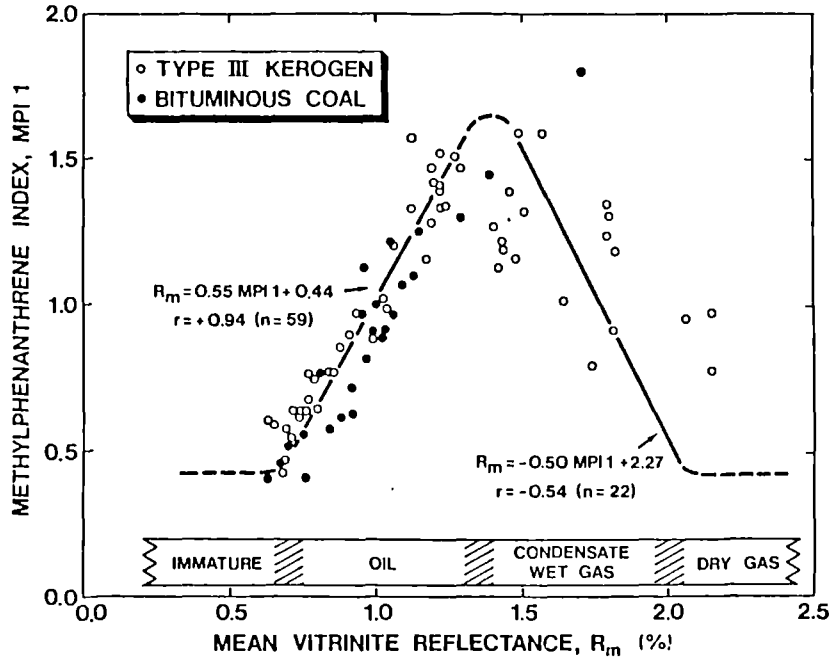


Fig.2.16 Calibration of the Methylphenanthrene Index (MPI 1) against mean vitrinite reflectance (R_m). Separate regression analyses were carried out for the samples with $\%R_m < 1.35$ and $\%R_m \geq 1.35$, respectively (modified from Radke 1987).

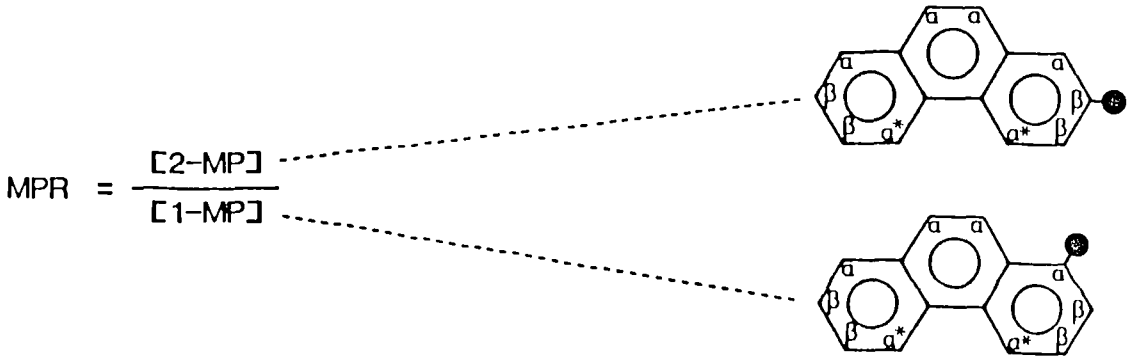


Fig.2.17 The methylphenanthrene ratio: structures and formula.

maturity of the source rock at the time of expulsion, providing that the original distribution of phenanthrene and methylphenanthrenes is retained during primary and secondary migration (Radke 1987, 1988).

Although the MPI was originally devised for bituminous coals in the West Canada Basin (Radke *et al.* 1982a), its success as a maturity parameter has been demonstrated in numerous sequences rich in type III kerogen (e.g. Radke and Welte 1983). The calibration of MPI and vitrinite reflectance for samples rich in other kerogen types has not, however, been successful due to the scarcity of phenanthrenes in type I and type II kerogens. The distribution of methylphenanthrene isomers seems to be governed by microbially-induced rather than thermally-induced transformations (Radke *et al.* 1986; Radke 1987, 1988). In addition to the methylphenanthrenes, the thermal evolution of aromatic hydrocarbon distributions can be assessed by monitoring trends in various alkylnaphthalene indices (reviewed by Radke 1987).

Naphthalenes are thought to derive from the aromatisation and degradation of terpenoid precursors present in micro-organisms and higher plants (see Strachan *et al.* 1988 for a review). Akin to the methylphenanthrenes, changes in alkylnaphthalene distribution are controlled by methyl-transfer reactions which lead to a reduction in steric strain within the molecule. Thus, the increase in methylnaphthalene ratio (MNR) with increasing rank is consistent with the proposed shift of α-methyl groups (1-MN) to β positions (2-MN) at elevated temperatures (Radke *et al.* 1982b). The same mechanism can also be envisaged for increases observed in the ethylnaphthalene ratio (2-EN/1-EN) with increasing rank. As Radke *et al.* (1982b) point out, the relative increase in abundance of 2-MN (and 2-EN) over 1-MN (and 1-EN) cannot be taken as unequivocal evidence for the conversion of the latter to the former because α-substituted methylnaphthalenes may be preferentially entering into other reactions besides rearrangement. This basis probably also holds for the conversion of dimethylnaphthalenes with two α methyl groups, i.e. 1,4-,1,5- and 1,8- dimethylnaphthalenes, as evidenced by their decrease with respect to the more stable αβ and ββ-type configurations with increasing maturity. Although several dimethylnaphthalene (DNR) ratios, based on the above transformations in response to thermal maturation, have been proposed (Radke *et al.* 1982b; Alexander *et al.* 1984a, 1985), that of Radke *et al.* (1982b) is the most commonly used:-

$$DNR1 = \frac{[2,6\text{-DMN}] + [2,7\text{-DMN}]}{[1,5\text{-DMN}]}$$

This ratio shows a closer correlation with reflectance than the MNR and appears to be less sensitive to source effects (Radke *et al.* 1984).

Changes in the relative abundance of α-substituted *versus* β-substituted positions analogous to those for DMNs have been reported in trimethylnaphthalene (TMN) distributions (Alexander *et al.* 1984a, 1985; Strachan *et al.* 1988). Of the ten TMN isomers commonly reported in sediments and petroleums, those with the greatest degree of substitution are most susceptible to rearrangement. The TNR-1 ratio, devised by Alexander *et al.* (1985), records the relative decrease of ααβ-substituted 1,4,6-TMN and 1,3,5-TMN with respect to the more stable ββββ substituted 2,3,6-TMN. A better correlation between the changes in TNR isomer distribution and vitrinite reflectance has been achieved by using the TNR-2 ratio (Radke *et al.* 1986; Radke 1987). The two ratios are:-

$$\text{TNR-1} = \frac{[2,3,6\text{-TMN}]}{[1,3,5\text{-TMN}] + [1,4,6\text{-TMN}]}$$

$$\text{TNR-2} = \frac{[1,3,7\text{-TMN}] + [2,3,6\text{-TMN}]}{[1,3,5\text{-TMN}] + [1,3,6\text{-TMN}] + [1,4,6\text{-TMN}]}$$

Enhanced relative abundances of 1,2,5- and 1,2,7-TMN have been documented in terrestrial samples of Cretaceous age and younger providing strong evidence for an origin from the degradation of higher-plant terpenoids for these isomers. The 1,2,7-TMN appears to be a specific marker for angiosperm contributions (Strachan *et al.* 1988); thus TMN distributions have some potential as specific organic-matter source indicators.

2.3.5 Geochemical Characteristics of Heat-Affected Organic Matter

Much geochemical work has been carried out in igneous-affected sedimentary sequences, mainly with a view to monitoring the changes in kerogen structure that occur with increasing proximity to the intrusions. Such studies have detailed the progressive modifications in elemental and isotopic compostitions as well as in nuclear magnetic resonance and electron spin resonance properties (Baker *et al.* 1977; Simoneit *et al.* 1978; Dennis *et al.* 1982; Jenden *et al.* 1982; Fredericks *et al.* 1985; Clayton and Bostick 1986; Ujiié 1986; Saxby and Stephenson 1987).

Relatively little consideration has been given to the study of soluble-extract data, and particularly to the detailed analysis of biomarker and aromatic hydrocarbon distributions. Of the studies that have investigated the changes in soluble-extract yields and their gross composition, the results are all broadly similar in that the thermal effects on bitumen are manifested by an increase followed by a decrease in EOM yield (corresponding to an oil window), increase in saturate/aromatic ratio, decrease in CPIs and isoprenoid/*n*-alkane ratios and a shift towards

front-end biased *n*-alkane distributions (Cory 1976; Dow 1977; Perregaard and Schiener 1979; Spiro 1984; Clayton and Bostick 1986; Saxby and Stephenson 1987). These observations generally parallel the thermal evolution of organic matter under the "normal" circumstances of temperature increase through burial and exposure to relatively long periods of geological time, although Altebäumer *et al.* (1983) did record a shift in the principal zone of hydrocarbon generation from $\%R_o$ =0.95, typical of "normally-matured" sequences, to $\%R_o$ =1.75 for a series of Liassic shales in the vicinity of the Bramsche Massif intrusion in NW Germany. Other deviations from conventional expectations were remarked upon by Rullkötter *et al.* (1982), Simoneit and Philp (1982) and Simoneit *et al.* (1984), who observed that some samples lying very close to intrusions of not inconsiderable size in the Guaymas Basin displayed no sign of geochemical alteration, either in the gross composition of soluble extracts or in biomarker distributions. Sediments adjacent to other intrusions in the same basin show the progressive isomerisation of immature ααα steranes and ββ hopanes into their thermodynamically more stable αββ and αβ counterparts with the S epimer dominating at the C-20 and C-22 chiral centres respectively. These changes in the steric configurations of saturated biomarkers have been reported in other heat-affected successions (Cory 1976; Spiro 1984; Gilbert *et al.* 1985).

There have been virtually no investigations into the changes in aromatic hydrocarbon distributions in igneous-affected sequences. Perregaard and Schiener (1979) noted that phenanthrene was the major aromatic component in heat-affected samples from a dyke locality in Greenland. Its formation was attributed to the cracking of cyclic triterpanes and steranes. Pyrene and chrysene were also documented, but no mention was made of their possible origin.

Simoneit *et al.* (1981) recorded high relative amounts of unsubstituted PAH in aromatic fractions of thermally-altered Cretaceous black shales in the eastern Atlantic for which a pyrolytic derivation was inferred. Suites of parent PAH have also been found in bitumen exudates from the Guaymas Basin which have been cited as evidence supporting a high-temperature origin for the petroliferous materials in this area (Simoneit and Lonsdale 1982; Simoneit 1984; Kawka and Simoneit 1987; Simoneit and Kawka 1987).

Mackenzie *et al.* (1988) charted the extent of aromatisation and cracking reactions in aromatic steroids in a suite of igneous-affected samples from NW Germany. These data, in conjunction with molecular-maturity ratios based on saturated biomarkers, were integrated with burial history curves to assess the extent to which rank imposition had been achieved through rapid heating from the Bramsche intrusion as opposed to deep burial. Apart from this work, there

have been no attempts to compare the sequential changes in polycyclic hydrocarbon distributions occurring through rapid heating as against those occurring through "normal" coalification. Altebäumer *et al.* (1983) did, however, note differences between CPI trends measured from samples associated with the Bramsche intrusion and from the "normally matured" Douala Basin, Cameroon.

2.4 HISTORY OF ORGANIC-RELATED RESEARCH IN THE MIDLAND VALLEY

2.4.1 Petrographic Characterisation of Organic Matter

The first organic petrological investigations arose from the famous lawsuit known as the Boghead Controversy in which legal action over the lease of land on which the Torbanehill torbanite was being mined made it imperative to determine whether the deposit was classed as a mineral or as a coal (Lyell 1853). Little conclusive evidence relating to the nature of the organic matter resulted from this intensive phase of study, and the so called "yellow bodies", of which the deposit was almost entirely composed, were attributed to the remains of plant tissues (Balfour 1854; Redfern 1855), bitumen globules or some other "combustible principle" impregnating a clay matrix (Quekett 1853; Bennett 1854).

Subsequently, more detailed examinations of this and other torbanites were undertaken by several workers, and for many years argument raged over the origin of the "yellow bodies". They were variously considered to have been derived from animal matter (Cadell 1901), spores (Jeffrey 1910), decomposed vegetable matter (Robertson 1912), dried-up petroleum globules (Cunningham-Craig 1916) or resins (Conacher 1917). An origin from algae was suggested as early as 1889 (David), but it was over three decades later before this view was universally accepted, largely because of a failure to comprehend how seemingly perishable algal material could survive and retain the fine morphological detail observed in many samples.

The algal theory was elaborated by Bertrand and Renault who, from the examination of many French and Australian torbanites, recognised two distinct algal-like morphologies which they termed *Pila* and *Reinschia* and which were later identified in Scottish torbanites (Renault 1899). Affinities of these forms to specific precursors were still not forthcoming, and this factor, coupled with inadequate explanations of how the presumed algae were preserved, proved prohibitive to the general acceptance of the algal theory at this time.

A major step forward occurred some years later when Zalessky (1914, 1926) specifically identified *Botryococcus braunii* as a potential precursor of the fossil algae in torbanites, but he did not back up his suggestion with any detailed morphological comparisons with living genera. Theissen (1925) had recognised that

the freshwater algae comprising the rubbery deposit, coorongite, bore a marked resemblance to algae in bogheads, although he misidentified the algae of which the coorongite was composed. The detailed comparisons between extant colonies of *Botryococcus* and the fossil algae in various bogheads were undertaken by Blackburn and Temperley (1936), whose work established unequivocally that the fossil *Pila* colonies are identical to the extant, freshwater, colonial alga *Botryococcus braunii.* The *Reinschia* colonies were considered to be polymorphic forms of *Botryococcus* despite suggestions by Bertrand (1930) that they might have originated from a different algal family. Both *Pila* and *Reinschia* have been described within the same sample of Torbanehill torbanite (Blackburn and Temperley 1936).

Although early work centred on their occurrence in torbanite, the "yellow bodies" had also been recognised in cannel coals and in the laminated oil shales of the Lothians Calciferous Sandstone Measures succession (Conacher 1917). In one of the most thorough early evaluations of the structure and composition of oil shales, Conacher (1917), from an examination of approximately 200 thin sections, identified the main constituents of the Lothians shales as carbonised plant fragments, miospores (occasionally), fossil fragments, mineral matter and "yellow bodies". The mixture was a fairly constant feature of the shales, but the proportions of the components varied from seam to seam. The bulk of the organic matter was found to consist of structureless material which gave the thin sections a brown tinge and was thought to represent "liquid putrefaction products of vegetable matter, the whole of the cellular structure having been obliterated". No further mention was made of this material. This paper also provides the first documented recognition that the petrographic composition of shales could be related to oil yield. Conacher made the empirical observation that an increase in the proportion of "yellow bodies" was accompanied by higher yields of distilled oil. Furthermore, as the proportion of the structureless "opaque groundmass" increased, so did the specific gravity of the oil.

Conacher (1917) also gave some consideration to depositional environments. In reiterating the brief interpretations of Carruthers *et al.* (1912), he inferred that the petrographic characteristics of the Lothians oil shales were consistent with a shallow-water origin and they were probably deposited on mudflats over which marine incursions were rare. The mode of formation of torbanites was given in more detail, and many of the interpretations formed the basis of later refinements. The lenticular nature of torbanite deposits and their occurrence within normal coal-bearing sequences was taken to indicate deposition in a swamp environment fringed with vegetation which filtered out all but the finest of material washed

into it. The water was judged to have been sufficiently deep to prohibit plant growth, which was restricted to the periphery of the swamp-pool in which accumulation of these debris resulted in the formation of "common" coal. Similar deductions were made by Cadell (1925).

In a subsequent paper, MacGregor (1938) assessed the characteristics of oil shales in relation to the sediments with which they were associated, enabling him to amplify the environmental interpretations of earlier authors, particularly in relation to the depositional environments of the Lothians oil shales. He concluded that the finely laminated nature of these oil shales, their high organic content and their frequent association with marly sediments, which sometimes had brecciated surfaces, all pointed to tranquil conditions of deposition in a slowly subsiding inland lagoon which was periodically subjected to desiccation and rarely had access to the sea that lay some distance to the east.

Later work, involving the study of oil-shale thin sections (Moore 1968) and of Lower Carboniferous patterns of sedimentation (Greensmith 1962, 1965, 1968), has built on the work of MacGregor (1938) by better defining organic- and inorganic-facies changes in the Midland Valley and by delimiting more precisely the extent of different depositional regimes, particularly within the Oil-Shale Group. These studies have also shed a little more light on the nature of the bulk of the organic matter comprising the Lothians oil shales. Greensmith (1962) recognised that the macroscopically discernible laminated nature of these sediments also persisted at the microscopic level, although the laminae (often only a few microns thick) were often irregular and were sometimes interrupted by carbonate layers. The carbonate layers impart a banded appearance to the rocks, clearly shown, along with the finely laminated nature of the shales, in the transmitted-light photomicrographs of Moore (1968). In this paper, reference is made to some of the organic-rich bands comprising "minute fragments of algal or fungal affinity" while the matrix of other oil shales is more poorly defined and comprises an "accumulated ooze". From this work the Lothians oil shales were inferred to have accumulated in a thermally stratified perennial lake.

In one of the most recent papers dealing with lacustrine sedimentation in the Midland Valley, Parnell (1988) has stated that the laminar organic material in the Lothians oil shales is equivalent to the lamalginite of Hutton *et al.*(1980) and Cook *et al.* (1981), although no petrological comparisons with known lamalginite-rich sediments were cited to support this judgment. Brief mention is also made of anastomosing bituminous films, also attributed to lamalginite, in organic-rich shales associated with the Burdiehouse Limestone (Loftus 1985; Loftus and Greensmith 1988). In the same publications these authors record similar material

in blackened, deep-water facies samples of the Burdiehouse Limestone which itself passes *into* oil-shale horizons. For some unstated reason, the assignment of these "films" in the Burdiehouse Limestone contradicts that made for the "films" in the oil shales (lamalginite) and is ascribed (in the limestone) to accumulations of *Botryococcus braunii*!

While these most recent papers provide "state of the art" information about depositional environments of the Lothians Oil-Shale Group and particularly on the Burdiehouse Limestone Formation, they do little to clarify the nature and origin of the various organic components within the Lothians oil shale *per se*. The lack of clarification stems largely from a failure to draw analogies, based on detailed organic petrological comparisons, with lacustrine oil shales in other parts of the world which display comparable petrological characteristics, where similar algal morphologies have been recognised and where the nature of the contributing organisms and their depositional environments have been well established. As a result, many of the statements in these recent papers (Parnell 1988; Loftus and Greensmith 1988) are conflicting, confusing and, as shown in Chapter 4, erroneous.

2.4.2 Chemical Characterisation of Oils and Soluble Extracts

Akin to the upsurge of interest in the petrographic evaluation of organic matter, the rise of the oil-shale industry also provided the initial impetus for the widespread chemical characterisation of organic materials, particularly shale oils. To maintain optimum efficiency of the retorts and to monitor the quality of the distilled oils required the frequent analysis of the retorted shale oils. Many data are incorporated in the industrially-related oil-shale literature which includes the results of analyses performed on whole oils as well as on their refined products (Carruthers *et al.* 1912, 1927; Conacher 1938; Stewart and Forbes 1938; Haresnape and Lowry 1952). Since oil quality and yield were ultimately governed by the properties of the raw material, variations in elemental analyses of oil shales and cannel coals have also been discussed, as have variations in the petrographic constitution of the sediments. As outlined in the last section, early studies established that higher oil yields were correlated with increasing amounts of "yellow bodies" (Conacher 1917; Skilling 1938), leading to the production of a lighter, less waxy shale oil (Carruthers *et al.* 1912, 1927; Conacher 1917). The highest yields were therefore achieved from the retorting of torbanites where yields, although generally around 120gals/ton (MacGregor 1938, Manson 1948), could exceed 140gals/ton in the most *Botryococcus*-rich samples (Skilling 1938). Increasing amounts of coaly components ("opaque groundmass" of Conacher 1917), characteristic of cannels, increased the wax content and reduced the yield of the

oils to between *c.*40-70gals/ton (Skilling 1938). The laminated oil shales of the Lothians yielded between *c.*15-25gals/ton (Stewart and Forbes 1938). Early work also established an empirical correlation between the proportion of hydrogen in oil shales and oil yield: lower C/H ratios gave rise to greater oil yields (Carruthers *et al.* 1927, p.167).

In addition to the analyses performed on retorted oils, chemical investigations were undertaken on "natural" oils, which were frequently encountered as seeps in oil-shale workings and were most commonly observed in the vicinity of igneous intrusions (Carruthers *et al.* 1912, 1927; Cadell 1925; Conacher 1925, 1932). This mode of association, coupled with numerous earlier recorded instances of bituminous and waxy materials occurring in the vugs and joints of mainly intrusive igneous rocks (Howell and Geikie 1861; Cadell 1898; Cadell 1901), led to a widely held opinion that many, if not all, of these petroleums were generated through the destructive distillation of carbonaceous shales that were invaded by high-temperature igneous materials (Cadell 1901; Peach *et al.* 1910; Carruthers *et al.* 1912, 1927; Conacher 1923, 1932; Cadell 1925). There were, however, many reports of free hydrocarbons occurring in areas in which there were no known occurrences of igneous rocks in the immediate locality (Steuart 1911; Carruthers *et al.* 1912, 1927; Conacher 1923, 1932; Tait 1926). Chemical analyses were therefore performed on many such petroleums and on industrially-retorted shale oils in an attempt to determine whether the former (igneous-unrelated) hydrocarbons were true high-temperature igneous distillates which would presumably (it was thought) possess chemical features characteristic of commercial shale oils (i.e. a high content of olefinic hydrocarbons). Results from the analyses of numerous oils revealed that, regardless of any proven association with igneous material, both groups of petroleums had markedly similar chemical compositions; sufficient to distinguish them from commercially-retorted crudes, but not sufficiently diagnostic to differentiate hydrocarbons found in the natural environment. Since the majority of analysed oils had been in close proximity to intrusions, the lack of differentiation was regarded as strong evidence favouring the igneous-induced generation of *all* free hydrocarbons in the Lothians oil-shale fields (Carruthers *et al.* 1912, 1927; Conacher 1923, 1932). The migration of igneous distillates, sometimes over many miles, was invoked to explain the presence of hydrocarbons in areas of the shale fields seemingly devoid of igneous activity (Cadell 1923; Conacher 1923, 1932).

Inclusion of the D'Arcy Oil in the suite of hydrocarbons investigated revealed that its compound-class constitution was virtually identical to that of oils found seeping from igneous intrusions, where an origin due to the contact of igneous material on organic-rich shales was considered to be beyond doubt (Conacher 1923; Carruthers *et al.* 1927). The similar chemical composition served to enforce the

view that hydrocarbons lying outside the oil-shale fields had also resulted from the effects of igneous intrusions on carbonaceous shales, despite their location in areas where igneous intrusions were comparatively rare.

The general applicability of igneous-induced hydrocarbon generation was queried in some publications. Steuart (1911) and Carruthers *et al.* (1912, 1927) suggested that at least some hydrocarbons could be natural petroleums *sensu stricto*, since the origin of many oils could not be linked with any igneous activity even when considering the possibility of migration (see above). Further evidence opposing hydrocarbon formation through igneous distillation was provided by Tait (1926), who considered that there were sufficient instances of oil spatially unrelated to intrusions for igneous activity not to be the cause of oil formation. He remarked that hydrocarbons had been found in virtually all parts of the Carboniferous succession in the Midland Valley and "occurrences of oil are as frequent, or perhaps more frequent, where there are no igneous intrusions, and are not confined to their proximity". Tait did, however, recognise the importance of igneous activity in producing black sandstones which had often been recorded in the vicinity of igneous intrusions (Forsyth 1846; Geikie 1902; Carruthers *et al.* 1912). On the basis of petrological examinations and laboratory-heating experiments, he inferred that black sandstones were derived from the burning, by igneous intrusions, of *pre-existing* oil-bearing reservoir sandstones to leave blackened sandstones; the colour imparted by the presence of a black, organic residuum. That many black sandstones were also petroliferous led Tait to suggest that oil migration into the sandstone had not only occurred prior to igneous activity, but had continued afterwards.

Notwithstanding the evidence favouring at least some hydrocarbon generation occurring independently of igneous activity, the opposing view still prevailed for many years, despite renewed consideration of chemical data including that relating to the D'Arcy Oil (Wyllie 1938). A cautionary note is appended to Wyllie's paper with a reference to the possibility that the move eastwards of increasingly marine conditions from the main oil-shale field might be conducive to the formation of marine sapropels of the type from which most of the world's petroleum is sourced and which might, locally, be transformed into petroleum without the intervention of igneous activity.

In one of the earliest widespread evaluations of onshore hydrocarbon reserves in the U.K., Lees and Cox (1937) state, on the basis of Conacher's (1923) work, "the possibility that no fluid oil is available other than that which has been distilled from shales by igneous action has been regarded as a deterrent from searching for an oil field in the Lothians". Subsequent published evaluations of U.K.

onshore reserves have not given any further consideration to the igneous *versus* non-igneous origin of hydrocarbon accumulations in the Midland Valley (Lees and Tait 1945; Kent 1985; Scott and Coulter 1987). A recent review of hydrocarbon occurrences in the Midland Valley has been given by Parnell (1984).

The earliest published literature dealing with organic chemical investigations of Midland Valley material in modern context relates to a paper by Douglas *et al.* (1969) which derives largely from a thesis by Maxwell (1967). The authors present the first gas chromatograms of the aliphatic hydrocarbon fractions of the Torbanehill torbanite and the Westwood Oil Shale. These analyses, coupled with gc-ms data, revealed the presence of isoprenoids and triterpanes in both samples: chemical evidence for an origin from biogenic precursors. Maxwell (1967) also examined a sample purported to be D'Arcy Oil collected from the D'Arcy well, Midlothian. Gas chromatographic analyses showed that the sample had an olefinic content higher than that of an industrial oil-shale distillate, which was also analysed, leaving no doubt that his sample of "D'Arcy Oil" was, in fact, a commercially retorted shale oil.

Douglas *et al.* (1970) later isolated carboxylic acids from the Torbanehill torbanite. Organic-extract data from this deposit and other *Botryococcus*-rich shales have subsequently been included in various geochemical projects undertaken in the Organic Chemistry Unit at Newcastle over the past few years (Allan 1975; Larter 1978; Allan *et al.* 1980; Muhamad 1986; Thompson 1987; Eglinton 1988). These shales have been used as classic examples of rocks rich in type I kerogen in projects which were not otherwise connected with the Midland Valley.

Cory (1976) described the qualitative changes in the distribution of various triterpanes and aromatics within the Killoch Coal as a contact with a whin dyke in the Mauchlin Basin was approached. Shifts in the distribution of *n*-alkanes were noted, as was the increased dominance of low molecular-weight aromatic hydrocarbons. Apart from CPI and Pr/Ph ratios, no other molecular measurements were made. Laboratory heating experiments were performed on unaltered samples of the Killoch Coal in an attempt to simulate rapid heating in the natural environment, but these experiments proved only partially successful.

Hall (1981) and Douglas *et al.* (1983) have included data from various Midland Valley oil shales, mainly from the Lothians, in a geochemical overview of European oil shales. No detailed integrated organic geochemical and petrological evaluation of the organic material was undertaken and relatively little consideration was given to the aromatic hydrocarbons. Further reference to this work is made in later chapters.

Bateson and Haszeldine (1986) have presented, in abstract form, preliminary results of a geochemical study designed to investigate type and maturity variations in biomarkers from 18 Dinantian oil shales. Plots of sterane carbon-number distributions were interpreted as indicative of terrestrial input. Although showing much scatter, maturation parameters determined in twelve oil shales from a succession at Mid Calder, intruded by a quartz-dolerite dyke, show a general increase in maturity approaching the dyke. Anomalously low values were recorded near the contact, but no explanation was given to account for this observation.

Details of the first geochemical study of a Midland Valley bitumen are included in the work of Robinson *et al.* (1986a), who examined the aliphatic hydrocarbon fraction of a bitumen associated with a quartz-dolerite dyke in the Hilderston borehole (Stephenson *et al.* 1983). Gc and gc-ms analyses revealed very low abundances of *n*-alkanes and acyclic isoprenoids superimposed on an unresolved hump. The major resolvable components were tricyclic hydrocarbons, hopanes and 8,14-secohopanes, the latter taken to infer a thermogenic origin for this bitumen. On pyrolysis, *n*-alkane generation was noted, but no further details were given.

The Hilderston bitumen was also included in a broader study involving the geochemical characterisation of British bitumens (Robinson *et al.* 1986b). Bitumens from Mid Calder, Dodhead and Uphall were investigated. Apart from the previously-published traces of the Hilderston bitumen, no other gas chromatograms or fragmentograms were included. The distributions of the various constituents were mentioned, but apart from an occasional Pr/Ph ratio, no molecular parameters were quoted. From these data it was concluded that "the compositions of the bitumens occurring in the Carboniferous strata of the Scottish Midland Valley are compatible with their origin from Lower Carboniferous oil shales". In an area that has experienced such a complex thermal history, such a conclusion must be highly suspect since it is based on analyses of only four, geographically widespread bitumens (that also occur in different geological settings) and only one postulated source rock.

2.4.3 Effects of Igneous Activity

As referred to in Section 2.2.5.1, the earliest known mention of the burning of strata as a consequence of igneous activity was by Sinclar (1672), this observation having been made on a Midland Valley coal which had been altered by a quartz-dolerite dyke at Prestongrange. This work also contains the first suggestion that intrusions may affect coals to differing degrees, since Sinclar remarked that the whin rock "renders the coal next to it, as if it were already burnt..." and yet "in others the coal is not altogether so ill".

Further observations on the extent of alteration were not apparently forthcoming until well over a century later, when Williams (1810; cited in Briggs 1935) noted that although burning in Scottish coals occurred to some distance either side of a dyke, its effect "is in proportion to the thickness of the dyke". He quotes a "rule" prevalent within the mining practice of the day which states that the extent of the "foul coal" adjacent to the dyke is found to be "nearly equal to one-half of its thickness".

Later notes on the variability of igneous influences were included in the first Geological Survey Memoir of Scotland (Howell and Geikie 1861) in which Geikie (p.115), referring to intrusions in the vicinity of Mid-Calder, commented that "the intrusive feldspathic rocks in this district produce much greater alteration in the strata than the augitic rocks".

Numerous other inconsistencies in the extent of thermal alteration are recorded, mainly as a result of observations made in the course of oil-shale mining. For example, Peach *et al.* (1910 p.278) describe the intrusion of an 80ft thick sill in the Broxburn shales near Newliston which has detroyed them, but has left them "uninjured" when it rises 50ft higher in the succession. Carruthers *et al.* (1912 p.15) fail to recognise any constant relationship between intrusion thickness and extent of alteration and cite the case of a 261ft thick sill at West Calder rendering only 6ft of "burnt blaes", the Broxburn shales some 35ft below being virtually unaffected. In contrast, over 300ft or more of strata have been burnt by intrusions in other parts of the West Lothian district, completely destroying the oil shales. On examining strata immediately beneath an olivine-dolerite intrusion in Hillhouse Quarry, Day (1928) remarked that there was no "special appearance of contact alteration".

Observations of carbonaceous sediments remaining apparently unaltered, when juxtaposed with igneous material, are generally associated with intrusives, but not exclusively so. Minimal alteration, if any, has been recorded with respect to plant and other sedimentary fragments found incorporated within volcanic necks (Geikie 1879; 1902; Balsillie 1920) and lava sheets. (Cadell 1892). On examining a mine exposure of the margin of the 700ft thick Gallowscrook vent near Philpstoun, Cadell (1898, 1901) noted that "there was little or no evidence of contact metamorphism or thermal action to be seen" and that "the oil shale was almost unaltered to within a foot or two of the neck".

The ability of igneous intrusions to alter variably organic-rich rocks was clearly recognised from the earliest geological observations in the area. Investigations geared towards determining the nature and extent of this alteration were largely restricted to the study of the mineralogical changes in the igneous rock

caused by contact with the country-rock rather than *vice versa*. In this respect much attention was given to the description and chemical characterisation of white-trap (Geikie 1879; Stecher 1888; Campbell and Stenhouse 1908; Day 1928), observed as a yellow-white, bleached zone and invariably found at the margins of intrusions which have penetrated carbonaceous shales.

Although the spotting of sediments at intrusive igneous contacts was frequently recorded and was attributed to "aggregates of chlorite or organic matters" (Peach *et al.*1910 p.314), more detailed investigations of the nature of thermal effects in the country rock, and particularly in carbonaceous sediments, were not undertaken until the chemical and physical analysis of coals was practised. Early published elemental and volatile-matter data were provided by Dron (1912). His results showed that, with increasing proximity to the Abbey Craig dolerite, volatile matter decreased so that the coal passed from unaltered, non-coking bituminous coals, to coking coals and finally to anthracites. These results supported a long-held view that anthracites in the Scottish coalfields were produced by the heating of bituminous coals by igneous intrusives, particularly sills (Dron 1917). That the occurrences of anthracitic coals, reported in various Geological Survey memoirs, are invariably associated with igneous intrusions bears witness to this opinion (Clough *et al.* 1916; MacGregor and Anderson 1923; Clough *et al.* 1925; Dinham and Haldane 1932; Robertson and Haldane 1937).

Clough *et al.* (1925 p.66) possibly made the first statement that the burning so often observed in Scottish coals occurred to a greater distance above a sill than below and confirmed observations made earlier that the distance over which the burning effect was felt was related to the thickness of the intrusion. No data were offered in support of this statement. The differential thermal alteration of seams with respect to distance above and below sills was considered by Briggs (1935). In citing examples from different parts of the world, he affirmed the observations of Clough *et al.* (1925) albeit in relation to anthracitisation rather than to burning. One example illustrating this phenomenon utilised the results of volatile-matter analyses from two suites of Midland Valley coals. Anthracitisation could be traced to a depth equivalent to less than half a sill's thickness below a sill in Queenslie Colliery (from map data; probably an alkaline dolerite), whilst at Manor Powis the effects of anthracitisation extended to a distance exceeding the thickness of the underlying Abbey Craig quartz-dolerite sill. Although this provides additional evidence of the vagaries in the extent of thermal alteration caused by intrusions in the Midland Valley, the data are not directly comparable; the coals analysed were taken from above the sill at Manor Powis and from below the sill at Queenslie, the locations

being geographically distinct and the sills being of different types and ages. Conclusions on the relative extent of anthracitisation above and below intrusions, if based on the Midland Valley data of Briggs (1935), are not therefore necessarily valid.

Robertson and Haldane (1937) did not find any evidence, based on volatile-matter analyses, lending support to the view that anthracitisation occurred to a greater distance above a sill than below it in the Kilsyth district, but they did note that a reduction in volatile content occurred in all coals as the Midland Valley sill was approached. The effect of the sill was noticeable to a distance of approximately one and a half times the sill thickness, although in one area thermal alteration was detected to a distance of five to six times. The presence of another underlying sill was assumed to have caused the latter, enhanced effect. In another area, at Auchinreoch, internal contortion and brecciation were noted in a coal near a whin contact; features recognised as typifying a coke rather than an anthracite. Robertson and Haldane concluded that "it cannot be doubted that the heat emanating from the whin has changed the constitution of the coal, resulting in a decrease in volatile matter. To this extent it may be said that the anthracitisation has been caused by the whin."

An alternative view for the cause of anthracitisation, at least in the Stirlingshire Coalfield was suggested by Skipsey (1959). He maintained that high-rank coals were produced by regional coalification due to the deep burial of strata to depths of 10,000ft along the downthrown side of the Ochil Fault. The thermal alteration of strata juxtaposed with igneous intrusions was considered to be much less important than previously believed. No further mention of Skipsey's paper is given in later publications, possibly due to the firmly entrenched belief that the close spatial association between anthracites and intrusions is sufficiently well established to preclude any other explanation for anthracite formation.

Anderson (1963) confirmed some of the observations of Dinham and Haldane (1937) by noting, in the Rashiehill Borehole, Stirlingshire, that the loss of volatiles brought about by the intrusion of the Midland Valley Sill into the succession is not detectable at a distance beyond one and a half times the sill thickness. In contrast to the findings of Dinham and Haldane, the thermal effects were found to be twice as great above the sill than below.

Despite the fact that reflected-light microscopy has been successfully applied for several decades in evaluating geothermal histories in many sedimentary basins elsewhere in the world, there is still a paucity of reflectance data relating to coal-bearing sequences in the Midland Valley. Chandra (1963) and Cory (1976) both included reflectance data from a few heat-affected samples of the Wilsontown

Main seam and the Killoch Coal respectively, as part of broader studies designed to compare the chemical and optical properties of thermally metamorphosed coals with those of normal coals.

The first organic petrographic and optical determinations on heat-affected dispersed sedimentary organic matter in the Midland Valley were undertaken by Raymond (1983). The textural characteristics of vitrinite, in combination with reflectance data, were used to elucidate different patterns of heat flow within the Rashiehill Borehole, allowing important conclusions on the timing of emplacement of the Midland Valley Sill. The optical analysis was also valuable in monitoring modifications of the molecular structure of vitrinite approaching igneous bodies. Since many conclusions reached in this study can be applied to other borehole sequences examined through the course of the current project, a detailed discussion of the results is deferred until a later chapter. The reflectance data elaborated the results of Anderson (1963), demonstrating that the extent of thermal alteration of organic matter above the Midland Valley Sill in this succession is three times greater than below it.

2.4.4 Lateral Rank Variation and Regional Coalification

Since so few rank data exist for the Midland Valley, from which to establish vertical and lateral maturity variations, whether a given rank has been imposed through igneous activity or through the "normal" means of regional coalification is difficult to decide unambiguously.

The National Coal Board (1960), now British Coal, produced a series of maps illustrating present-day rank variation within the Scottish Coalfields, devised from a combination of volatile-matter content and coking characteristics. On this basis it is apparent that the rank at a given stratigraphic level increases moving from the Fife Coalfield towards the Central Coalfield. It cannot be ascertained whether this variation is due to an increase in geothermal gradient moving westwards or whether the rank further to the west has been enhanced due to igneous activity or because of a combination of both factors.

Optical analyses of coals in the studies of Chandra (1963) and Cory (1976) suggest that some samples may lie outside the thermal aureoles of igneous intrusives. Reflectance values determined on samples most distant from the intrusions still indicate relatively high ranks (*c*0.70-0.90%VR). In the absence of data from adjacent localities, it cannot be established if these reflectances represent true background maturation levels or if they also have been subjected to thermal influence by other intrusives. Given the pervasive nature of igneous acitivity in the Scottish coalfields, the second possibility is not unlikely.

National Coal Board analyses (excluding reflectances) are available for several seams selected from boreholes in east Fife (Forsyth and Chisholm 1968), which show the coals to be high-volatile and non-caking. The general similarity between the analyses, coupled with the fact that the coals do not appear to be closely associated with igneous bodies, suggests that the determinations are indicating the true background maturity level. Reflectance measurements on three samples of Westfield Oil Shale were included in the paper of Hutton *et al.* (1980) as and illustration of suppression effects (Section 2.2.4.1.2.3). On the basis of the limited data in this paper, the true maturation level of the Westfield Oil Shale cannot convincingly be established, since the presence of significant quantities of algae has led to an overprinting of the true, unsuppressed rank.

Penetration of the igneous-affected succession in the Rashiehill borehole was sufficiently deep to permit the construction of a background-reflectance profile. This study provided the first information on the extent to which background maturation gradients have been modified by igneous activity in the Midland Valley. Further discussion of this study is given in later sections.

2.5 AIMS OF THIS THESIS

Given the long history of commercial interest in the exploitation of coal, oil shale and hydrocarbons in the Midland Valley, it is surprising that, even with the major advances that have taken place in the field of organic geochemistry and organic petrology over the past two decades, there is still little published information on the type and maturity of organic matter in this province. Much of the existing literature provides data that were generated in response to the requirements of the oil-shale and coal-mining industries. The subsequent decline in these industries was accompanied by reduced interest in organic-related investigations. Despite the proven success of "modern" organic petrological and geochemical methods in defining the type and maturity of organic matter in sedimentary basins, this review illustrates that the application of these techniques has been minimal in successions of the Midland Valley.

The interplay between tectonics, volcanism and sedimentation was instrumental in creating many different depositional milieux, both spatially and temporally, within the Carboniferous of the Midland Valley. Notwithstanding the potential diversity of organic materials which could accumulate in the various environments, modern organic-related investigations have focused on lacustrine deposits (mainly torbanites), while marine and deltaic facies, long known to contain abundant organic matter, have been ignored. Furthermore, although the capricious manner in which igneous material modifies the properties of carbonaceous

sediments has been alluded to for over 300 years, no unifying theory has been advanced in the Scottish literature (or any other for that matter) to account for this.

In the light of the paucity of organic geochemical and petrological studies in what, after all, has long been recognised as a potential petroleum province, it is clear that the Midland Valley would benefit from investigations more thorough and broadbased than those so far undertaken. The main objective of this thesis, therefore, has been to conduct an organic geochemical and petrological evaluation of the variation in organic-matter type and maturity within the Carboniferous succession of the eastern and central Midland Valley of Scotland and to investigate the extent to which the geochemical and optical properties of the organic matter have been modified by igneous activity. Several aspects are considered as outlined below:-

(i) optical and geochemical characterisation of different types of organic matter contributing to the sediments and detection of any palaeoenvironmental changes both spatially and as a function of time;

(ii) analysis of bitumens and oils taken from oil wells and outcrops, with a view to establishing (a) whether they represent igneous distillates or "natural" petroleums; and (b) source-rock correlation(s);

(iii) evaluation of present-day rank variation by (a) constructing rank maps, based on vitrinite reflectance data, for different stratigraphic horizons throughout the Carboniferous to establish lateral maturation patterns and their variation through time; (b) constructing borehole reflectance profiles to determine vertical rank gradients and their variation throughout the area; and (c) integrating (a) and (b) with lithological data from borehole logs to assess the extent to which the present maturation levels are attributable to the effects of intrusive and extrusive igneous activity, as opposed to regional coalification brought about by the "normal" background geothermal gradient;

(iv) utilisation of the optical and textural characteristics of vitrinite to delineate the timing of emplacement of the Midland Valley Sill and other intrusions with respect to the regional level of maturation, which has important implications for the timing of hydrocarbon generation

and enables deductions to be made on the influence of igneous activity on hydrocarbon generation in the Midland Valley; and

(v) evaluation of the extent to which various type- and maturity-dependent geochemical parameters are affected by igneous activity and regional coalification.

To maintain a geological perspective, the geochemical and petrological data are integrated and interpreted in the light of the known geological history of the area to achieve a greater understanding of organic-matter type and maturity variation within the Carboniferous succession of the Midland Valley of Scotland.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 SAMPLE COLLECTION

The majority of sediment samples used in this project were obtained from various rock collections lodged with the British Geological Survey in Edinburgh. Most of the coals were sampled from the palynological collection held by the National Coal Board at Wath-upon-Dearne, Yorkshire. The collection of field samples was restricted mainly to coastal sections as inland exposure was generally very poor. Additional samples were provided by oil companies and individuals. The origin of all specimens is indicated at the end of each batch of sample descriptions in Appendix I.

Weathering has been shown to affect the geochemical properties of organic-rich sediments adversely, both in terms of the reduction in the absolute concentration of organic matter present and also in the depletion of "light ends" (Leythaeuser 1973; Clayton and Swetland 1978; Forsberg and Bjorøy 1983). Molecular parameters based on polycyclic saturated and aromatic compounds may also be affected (Clayton and King 1987). Every attempt was made, therefore, to circumvent, or at least minimise, the problem of weathering by collecting fresh field samples from as great a depth as possible within a given surface exposure. Coastal samples were preferentially collected from as high above the high-water mark as possible, avoiding material adjacent to joints and fissures. The samples were wrapped in aluminium foil ready for laboratory analysis.

3.2 ORGANIC PETROLOGY

3.2.1 Sample Preparation

Mud-covered field and core samples were rinsed with tap water and the outer surfaces were removed with a wire brush. Oil-company cuttings samples which had been received directly from the well site were water-washed to remove drilling mud and then sieved and picked to remove caved material. All samples were dried prior to further preparation.

Samples for reflected-light and fluorescence microscopy were crushed with a pestle and mortar and the chips were mounted in a slow-setting epoxy resin. After hardening, the samples were rough ground on a diamond lap to expose the surfaces of the particles and then fine ground on 280 and 600 grade silicon carbide papers. Polishing was performed on "Selvyt" cloth-covered laps using successively finer grades of corundum powder (5/20, 3/50 and "gamma" grades). Water was used as the polishing medium for coals and carbargilites whilst isopropyl alcohol (IPA) was used for sediments. The use of IPA prevents the swelling of clay minerals which would occur if water were used as the lubricant for sediment polishing.

Standard 30μm thick thin sections and kerogen strew mounts were prepared for viewing in transmitted light.

3.2.2 Reflected-Light Microscopy

3.2.2.1 Equipment

A Zeiss "Standard Universal" microscope was used for reflected-light microscopy and was fitted either with strain-free Epiplan or Antiflex Epiplan polarising objectives depending on requirements. The output from a photomultiplier (EMI 9844A, Venetian-blind type) was fed to a Philips PM8200 pen recorder. Both the photomultiplier and tungsten filament lamp (12V, 60W) received stabilised electrical supplies. The microscope set-up is shown in Fig.3.1 and Plate 3.1.

Throughout the course of this work, the glass-plate reflector (coated cover slip) was used as the vertical illuminator in preference to the Berek prism, despite the fact that it induces rotation of the vibration direction of the light rays. Its use was justified on the grounds that it facilitated the identification of primary vitrinite because the relationship between the vitrinite and the surrounding matrix could be discerned more readily, particularly in high-rank sediments. This improvement was due to the symmetrical illumination provided by the reflector as opposed to the oblique illumination afforded by the Berek prism, the latter accentuating the relief of phytoclasts thereby hindering identification. The overall error induced by not satisfying the optimum optical conditions was considered to be less than that which would be incurred through misidentification of the vitrinite component, which might have arisen through using the Berek prism. Other errors inherent in the determination of vitrinite reflectance are shown in Table 3.1 which is modified from Raymond (1983) and which was compiled from Piller and von Gehlen (1964), Cook and Murchison (1972), Goldring and Juckes (1972), Galopin and Henry (1972), Piller (1977) and Embrey and Criddle (1978). All possible precautions were taken to obviate or at least minimise errors.

3.2.2.2 Measuring Procedure

Reflectances were determined under oil immersion at 546 nm on up to 20 indigenous vitrinite clasts. In sediments these were present as wispy entities or elongate stringers. In some cases, fewer measurements had to be accepted owing to the paucity of vitrinite in some samples. Reflectances were meaned to give sample rank.

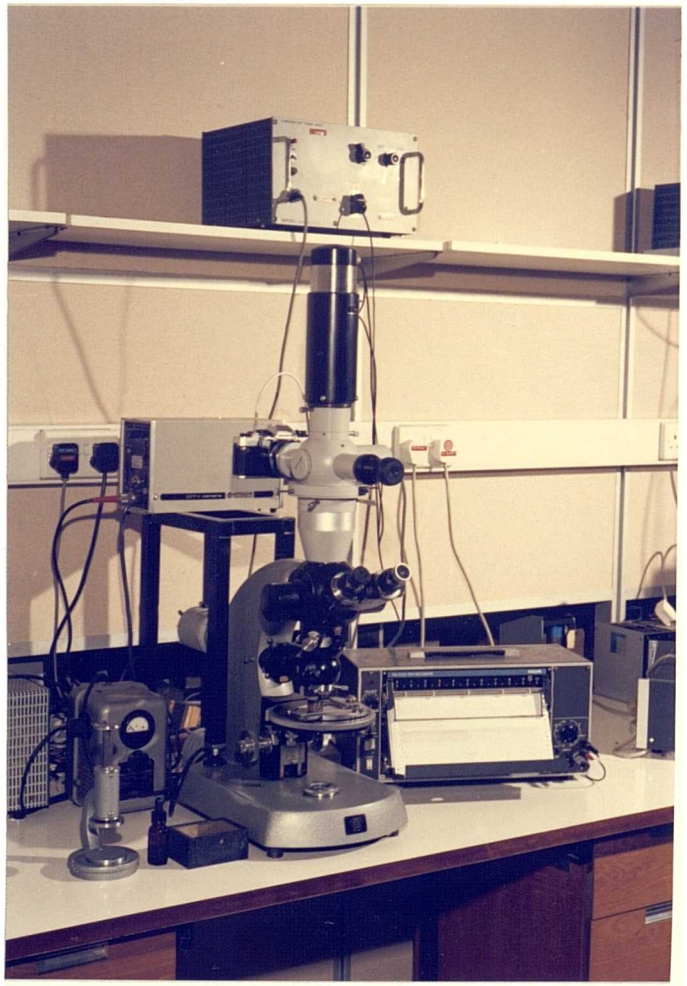


Plate 3.1 Microscope photometer.

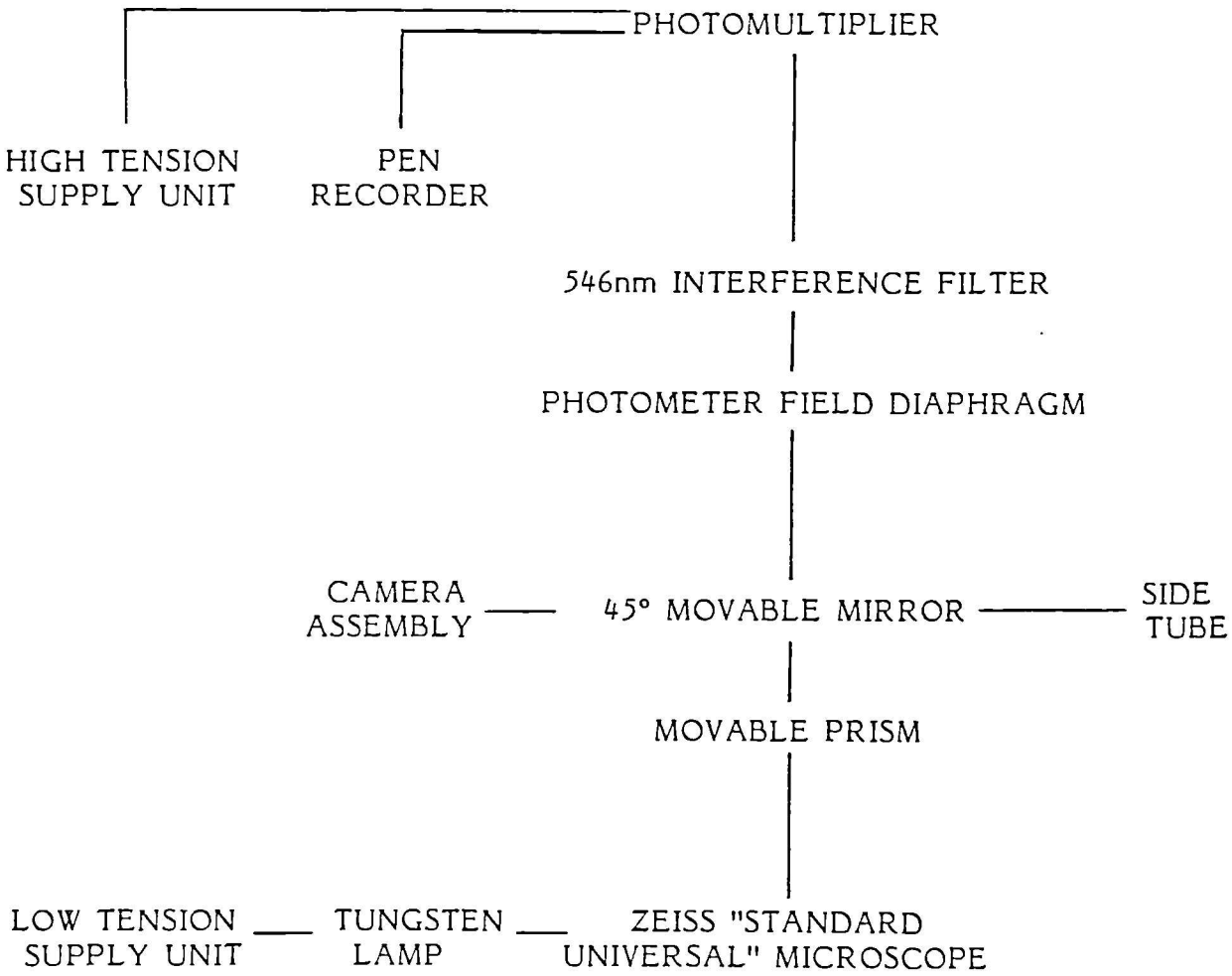


Fig.3.1 Schematic representation of reflectance apparatus.

Table 3.1 Reflectance errors and their correction.

SOURCE OF ERROR	CORRECTION
OPTICAL CONDITIONS OF THE MICROSCOPE	
DISTURBANCES OF THE LIGHT TRAIN	Ensure : no mechanical vibrations no fluctuations in the illuminating beam correct centring of microscope elements
GLARE - due to internal scattering of light at lens mountings, cemented lens surfaces, inner tube walls, etc.	Ensure : correct adjustment of field and photometer irises use of lenses with dielectric coatings correct centring of microscope elements
NON-LINEARITY OF PHOTOMULTIPLIER AND PEN RECORDER	Ensure standards are correctly adjusted to the electrical systems
DARK CURRENT - permanent electric current caused by thermionic emissions from cathode	Can be ignored in high quality tubes where it is usually less than 1% - if substantial, deduct the deflection induced on the pen recorder from all reflectance determinations
FILTER giving too great a dispersion	Use a filter with as narrow a band pass width as possible so that the minimum dispersion of results about 546nm is attained
POLARISER incorrectly adjusted	Orientate polariser in accordance with the optical requirements of the vertical illuminator *viz.* zero with plate glass reflector, 45° position with Berek prism

SOURCE OF ERROR	CORRECTION
SPECIMEN	
UNDER-POLISHING - leaves scratches resulting in artificially low readings OVER-POLISHING - increases relief of photoclasts leading to off-axial reflections	Optimum polish
UNLEVELLED SPECIMEN - gives (i) eccentric oscillation on rotation of stage leading to loss of focus; (ii) reflectance at normal incidence not maintained	Careful mounting with hand press to ensure specimen surface is perpendicular to microscope optic axis - check rotation in back focal plane of objective
MATRIX GLARE e.g. vitrinite in chalk. Overwhelming whiteness of chalk matrix may lead to glaring of small vitrinite particles	Close field and photometer irises to reduce glare to minimum
IMMERSION OIL	
TEMPERATURE FLUCTUATIONS - (i) rise in temperature lowers refractive index thereby raising reflectance; (ii) change in refractive index reduces resolution of the objective since the front lens is corrected for a specific value of n	Maintain constant temperature in immersion medium
AIR BUBBLES - obscure field of view	Wipe oil from objective and refocus
OPERATOR	
INCORRECT FOCUSING - outside depth of focus, a small change in distance between specimen and object gives a large change in reflectance readings	Careful focusing

SOURCE OF ERROR	CORRECTION
INCORRECT CHOICE OF STANDARD - Large differences in reflectance between standard and specimen give large errors - worst case is using a high reflectance specimen with a low reflectance standard	Choose standard with a similar reflectance to specimen. Best choice is a standard of slightly greater reflectance than the specimen
BIASED CHOICE OF PARTICLES	Measure reflectance on a range of vitrinitic material in the sample
MISIDENTIFICATION OF THE VITRINITE COMPONENT	Train the operator

A x40/0.85 oil-immersion objective was employed throughout the measuring procedure in conjunction with a x10 eyepiece and Zeiss immersion oil of refractive index 1.518 at 23°C. Vitrinite reflectance was determined by comparing the intensity of light reflected from the vitrinite clasts with that reflected from a standard of known reflectance. The substitution of the appropriate values into the following equation enabled the calculation of the vitrinite reflectance value:-

$$Ru = Rs \times \frac{Du}{Ds}$$

where : Ru = reflectance (as %) of vitrinite

Rs = reflectance (as %) of standard

Du = deflection (in scale divisions) of pen recorder measuring vitrinite

Ds = deflection (in scale divisions) of pen recorder measuring standard

The standards used had the following reflectances at 546nm under oil immersion:-

Sapphire	0.590%
Yttrium Aluminium Garnet (YAG)	0.917%
Cubic Zirconia	3.341%
Diamond	5.230%

To circumvent the effects of host-rock lithology on vitrinite reflectance (Section 2.2.4.2.2.2), measurements were restricted, where possible, to argillaceous sediments or coals. $R_o$max values were quoted for coals analysed in the early stages of the project, but the time-consuming nature of the determination led, later, to the exclusive use of $R_o$average ($R_o$av). At the level of rank encountered in the sequences in which $R_o$max was measured, $R_o$max and $R_o$av correspond.

3.2.3 Fluorescence Microscopy

Fluorescence microscopy was carried out on a Zeiss "Standard Universal" microscope to which a HBO 200W high pressure mercury lamp was attached. Fluorescence was induced under blue-light excitation using a Zeiss KP 490 exciter filter in conjunction with a dichroic mirror with a reflectance edge of 500nm. A 530nm barrier filter was used as a safety measure to prevent any stray short-wave radiation from reaching the eye.

For the qualitative assessment of sample maturity, based on spore fluorescence properties, undertaken in this project, the "in house" guidelines shown in Table 3.2 were employed.

Table 3.2 Correlation of qualitative fluorescence parameters with vitrinite reflectance.

Spore Fluorescence Colour	Vitrinite Reflectance(%) (546nm)	Fluorescence Intensity	Sample Maturity
green	0.25	Intense	Immature
green/yellow	0.30		
yellow			
orange/yellow	0.40		
yellow/orange	0.50	Moderate	
light orange	0.60		Mature
	0.65		
mid-orange	0.70	Dull	
	0.75		
deep orange	0.80		
red	1.00		
none	1.30	Extinct	Overmature

3.2.4 Transmitted-Light Microscopy

Transmitted-light examination was performed on a Zeiss "Standard Universal" microscope using a range of air objectives attached to a rotating turret.

3.2.5 Photomicrography

Reflected-light and transmitted-light photomicrography was performed using either an Olympus OM1O or a Zeiss MC63 camera body. Kodak Ektachrome 160ASA "Professional" (tungsten) film was used for prints in conjunction with a Kodak daylight correction filter. Black and white prints were obtained from Ilford "Pan F" 50 ASA film.

Photomicrography under fluorescence-mode illumination was carried out with a Zeiss MC63 camera body using either Kodak "Ektachrome" 160 or 200 ASA slide film or any 200ASA colour print film.

Both Epiplan strain-free and "Antiflex" objectives were employed. The different optical conditions are given adjacent to the plates in the text.

3.3 ORGANIC GEOCHEMISTRY

In addition to the valuable information gleaned from optical examination *per se*, the microscope was employed as a screening tool for geochemical work. Samples for geochemical analysis were selected on the basis of their organic content, organic-matter type and maturity determined from microscopy.

Utmost attention was given to the problem of contamination. All solvents were redistilled in a 30-plate Oldershaw column. The purity of each batch was checked by evaporating 250ml of solvent down to c10ml and analysing this concentrate by gas chromatography.

All copper turnings, adsorbents, cotton wool and extraction thimbles were pre-extracted for 24 hours using dichloromethane (DCM). Glassware was steeped in chromic acid overnight, rinsed with distilled water and then oven-dried. Before use, the glassware was rinsed with the solvent to be used.

3.3.1 Sample Preparation

In the laboratory, field and core samples were rinsed with water whilst the outer surfaces were removed with a hard wire brush. The specimens were then broken into pieces, placed in a beaker, covered with methanol and ultrasonically washed for fifteen minutes. The chips were then dried and crushed in a disc mill ("Tema") ready for soxhlet extraction.

Pre-washed, sieved and picked oil company cuttings samples were ultrasonically washed for three minutes, dried and finely ground with a pestle and mortar.

The inner surfaces of hard and soft bitumens, which were found in vugs and coating joints in some samples, were chipped and pared, respectively, from the host rock with a clean knife and wrapped in aluminium foil prior to analysis.

3.3.2 Extraction Procedure

Up to c.100g of powdered rock or bitumen were placed in a cellulose thimble and soxhlet-extracted with an azeotropic mixture of DCM and methanol (93:7) for 72 hours. Activated copper turnings were added to the extraction flask to remove elemental sulphur. The total extractable organic matter (EOM) was concentrated using a Buchi evaporator and transferred to a pre-weighed 100ml, 50ml or 25ml flask, depending on the EOM yield. The remaining solvent was removed under reduced pressure and the total EOM was weighed and then stored, under solvent, in vials.

3.3.3 Thin-Layer Chromatography (TLC)

Initial fractionation of the EOM was achieved using thin-layer chromatography (TLC) which was performed using glass plates (20cm x 20cm) that had been thoroughly washed with hot detergent, rinsed and dried prior to use. The plates were coated with an aqueous slurry of silica gel (Merck 60G "Kiesel Gel") which, on drying, gave plates with a phase thickness 0.5mm. After activating in a drying

oven at 120°C (2 hours), the plates were re-cleaned by developing in ethyl acetate and returned to the oven for reactivation.

Samples were spotted on to the plates using fine capillary tubing together with four standards : *n*-hexadecane (aliphatic; R_f=0.79), 1-phenyldodecane (mono-aromatic; R_f=0.48), anthracene (triaromatic; R_f=0.19) and perylene (tetra-aromatic; R_f=0.10). The plates were then developed in petroleum ether and viewed in UV light after spraying with a methanolic solution of "Rhodamine 6G". Bands containing the aliphatic and total aromatic fractions (1-phenyldodecane $\geq R_f \geq$ perylene) were scraped from the plate into short columns containing *c*2cm of activated alumina. The hydrocarbons were desorbed by eluting with 50ml of petroleum ether and DCM (4:1, aliphatics; 1:1, aromatics). The remaining material on the plate comprised the polar fraction.

Plates were run in duplicate. To obtain an accurate weight for each fraction, *c*20mg of EOM were spotted on to the plate and the recovered aliphatic and aromatic fractions were evaporated to *c*1ml with a Buchi, transferred to a pre-weighed vial and blown to dryness in a stream of nitrogen. The polar fraction was calculated by difference. Approximately the same amount of extract was loaded directly on to another plate and the hydrocarbon fractions were obtained without blowing down, thus preserving the original hydrocarbon distribution which had, hopefully, been unaffected by the laboratory work-up procedures. These fractions were used for gas chromatography (gc) and gas chromatography-mass spectrometry (gc-ms).

For the separation of saturated from unsaturated aliphatic hydrocarbons, argentation TLC was performed using a composition of aqueous slurry modified by adding 10% silver nitrate. The aliphatic fraction and two standards (*n*-hexadecane and *n*-hexadecene) were loaded on to the plate and developed as described above. The unsaturated material was removed at R_f<0.60.

3.3.4 Urea Adduction

Urea adduction provides a rapid means of separating normal and simple-branched (usually iso- and anteiso alkanes) from multi-branched and cyclic alkanes. This method was utilised on many samples in the early stages of the project to aid compound identification, but was only performed thereafter to concentrate the biomarker components in samples containing very low abundances of these compounds relative to *n*-alkanes, so enabling the acquisition of satisfactory biomarker mass spectral data.

Approximately 3-4mg of saturated hydrocarbon fraction was dissolved in petroleum ether/acetone (2:1, 2-4ml) in a small centrifuge tube. Approximately 0.5-1.0ml of urea-saturated methanol was added dropwise whilst gently agitating the centrifuge tube. The resulting precipitate contained clathrated normal and simple-branched alkanes, whilst the non-adducted components remained in the solvent. The solvent was evaporated in a steady stream of nitrogen and the process repeated twice. The non-adducted hydrocarbons were dissolved in 3-5ml of petroleum ether and were pipetted off after centrifugation at 3000rpm for five minutes. The operation was repeated twice. The adducted hydrocarbons were retrieved by dissolving the urea crystals in distilled water (2ml) and successively extracting the aqueus solution with petroleum ether (3x10ml). Any remaining water was removed by passing the petroleum ether containing the adduct through a short column containing activated alumina.

3.3.5 Gas Chromatography (GC)

Gas chromatography of hydrocarbon fractions was performed on one of two instruments: a Carlo Erba 4160 or 5160-mega series gas chromatograph equipped with an air-cooled, on-column capillary injector and a flame ionisation detector (FID).

Saturated and aliphatic fractions were separated on a fused silica column (50m x 0.32mm i.d.) coated with OV-1 (methyl silicone). Hydrogen was used as the carrier gas (pressure 0.9kg/cm^2) with the flow rate adjusted to 1ml per minute. The FID was maintained at a temperature of 300°C with hydrogen and air pressures of 0.5kg/cm^2 and 1kg/cm^2 respectively. Temperature programming was from 50-290°C for the 4160 model and 50-300°C for the 5160-mega machine, both at a rate of 4°C/min with a final temperature hold of 25 minutes.

Aromatic hydrocarbons were fractionated using a fused silica column (25m x 0.3mm i.d.) coated with OV-101 (5% phenylmethylsilicone). A temperature programme of 50-300°C at 4°C/min was employed with a final hold time of 25 minutes. Other conditions were as above.

3.3.6 Gas Chromatography - Mass Spectrometry (GC-MS)

Gc-ms of hydrocarbon fractions was carried out on a Hewlett Packard 5890 gas chromatograph interfaced to a HP5970 series MSD quadrupole mass spectrometer (ionisation energy 70eV; filament current 220μA; acceleration voltage 2-3kV; source temperature 220°C).

A 25m x 0.2mm i.d. HP Ultra 1 column (methylsilicone) was used for the analysis of saturates and a 25m x 0.2mm i.d. HP5 (5% phenylmethylsilicone) column was used for aromatics. Split-splitless injection was employed with helium as the carrier gas. The gc oven was programmed from 40-300°C at 4°C/min with final hold times of 20 minutes (aliphatics) and 30 minutes (aromatics). Samples were analysed in both scan (50-500 amu; scantime 1.1s) and selected ion monitoring (SIM) modes (dwell time 40ms per ion).

3.3.7 Compound Identification

The hydrocarbon fractions retrieved through the work-up procedures described above provided the first indications of their identity in that the functionality of the unknown compound classes could be deduced from thin-layer chromatography (i.e. whether saturated or aromatic), whilst the extent of branching was indicated by urea adduction. The specific identification of individual components was only possible, following gc and gc-ms analysis, by comparing their retention times and mass spectra with those available in the literature. Spectral interpretation was attempted in some cases.

The basis for the identification of the main hydrocarbon compound classes encountered throughout the course of the current work is outlined below. The identification of more restricted or specific components is dealt with in the appropriate section of results.

3.3.7.1 Acyclic Alkanes and Short-Chain Isoprenoids ($\leq C_{20}$)

The ubiquity and abundance of these components and their occurrence in homologous series means that they are readily detectable by gc alone. Compound identification was therefore achieved by comparing retention times with published literature data.

3.3.7.2 Polycyclic Alkanes

These compounds relied on gc-ms for their identification, through the monitoring of fragment ions characteristic of the particular class of compound under examination. Unless otherwise stated, information on diagnostic fragmentation pathways within each class of biomarkers can be found in the relevant references cited in Section 2.3.3.

3.3.7.2.1 Bicyclics

The major fragment ion for this group of compounds has a mass-charge ratio (m/z) of 123, derived from the cleavage of two fused saturated rings (Fig.3.2 a).

Other diagnostic fragmentation pathways for bicyclics give rise to ions with m/z 109, 137 and 193 (Fig.3.2 b).

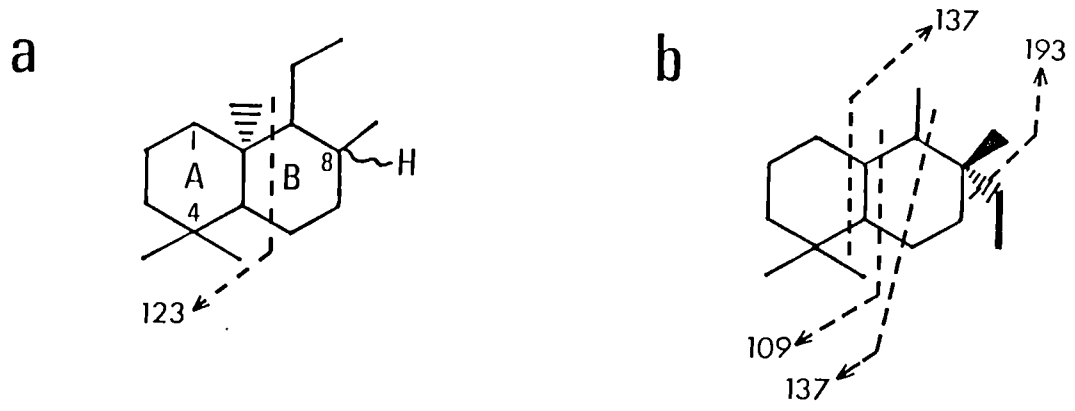


Fig.3.2 Diagnostic fragment ions for bicyclic alkanes.

3.3.7.2.2 Tricyclics and Tetracyclics

Distributions of tricyclic and tetracyclic terpanes can be monitored using m/z 191 which arises from the fragmentation pathways shown in Fig.3.3.

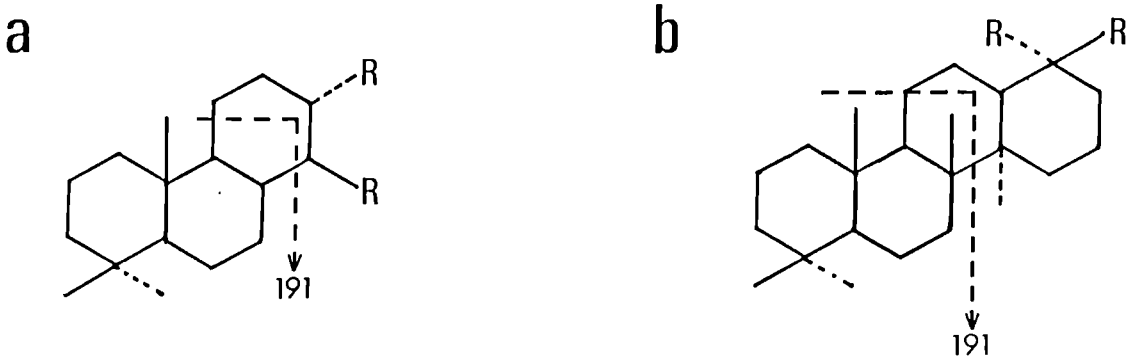


Fig.3.3 Fragmentation of tricyclic and tetracyclic alkanes.

3.3.7.2.3 Pentacyclic Triterpanes of the Hopane Series

Hopanes are relatively easy to detect and identify by virtue of the formation of two major fragment ions. The diagnostic fragment ion at m/z 191 is derived from the cleavage of the A/B ring fragment (Fig.3.4). The second major ion originates from the D/E ring systems plus the side chain R (i.e. ion at 148+R). Hence this ion will have the value of 149, 163, 177, 191, 205 ...depending on whether R = H, CH_3, C_2H_5, C_3H_7, C_4H_9 etc. Information on the stereochemistry

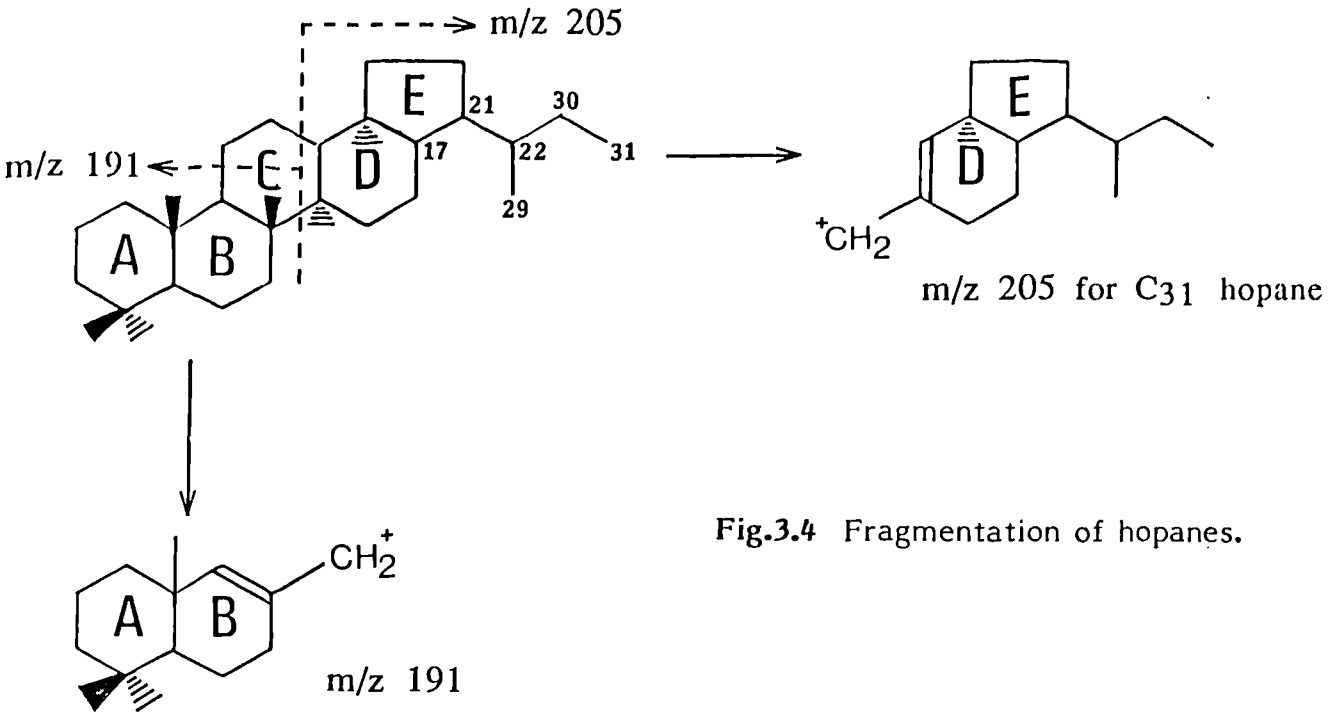


Fig.3.4 Fragmentation of hopanes.

at the C-17 and C-21 positions of the parent molecule can be determined by monitoring the relative intensity of these ions. The spectral characteristics for different hopane series are summarised below:-

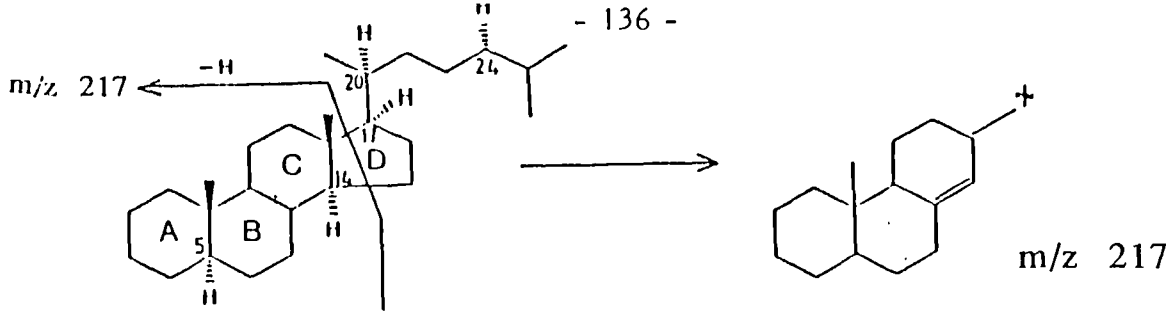
Hopane Stereochemistry	m/z intensity
ββ	191 < 148 + R
αβ	191 > 148 + R
ββ	191 ≈ 148 + R

Resolution of the stereochemistry at C-22 was not possible on the basis of mass spectrometry, thus the S and R isomers were distinguished on the basis of elution order (22S isomers elute before 22R).

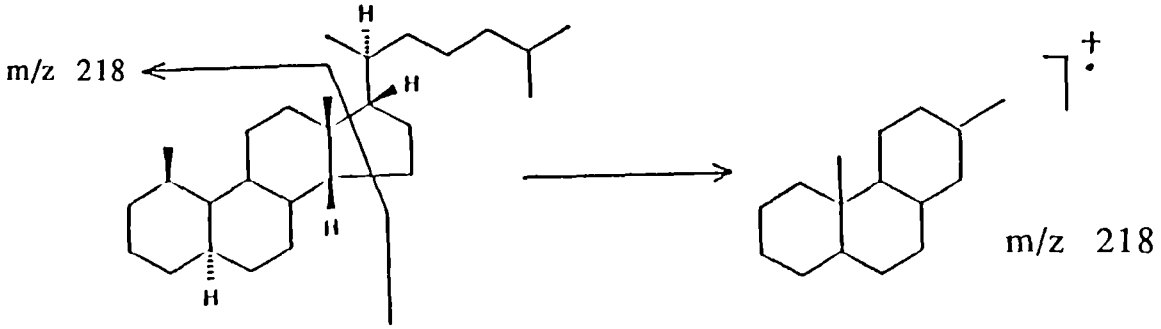
Modifications to the ion series used for monitoring the demethylated and methylated hopanes are required : removal of the C-10 methyl group in the former means that the A/B rings now give major fragments with m/z 177, whilst the additional methyl group in the A or B ring requires the use of m/z 205 instead of m/z 191 to detect the methyl hopanes.

3.3.7.2.4 Steroidal Hydrocarbons

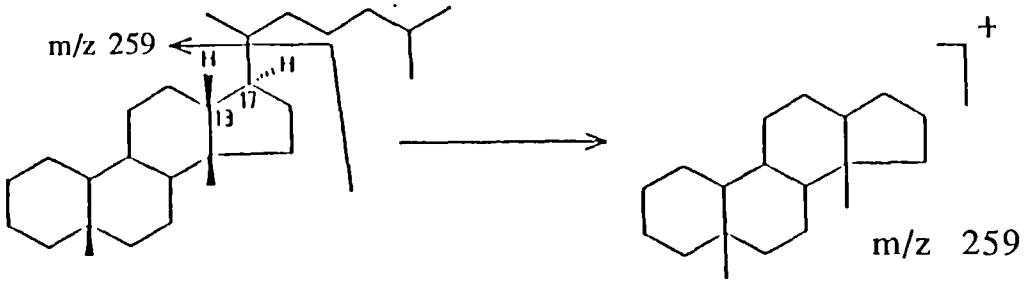
The characteristic fragment ion used to detect the regular steranes is m/z 217, which corresponds to the ABC ring system (Fig.3.5a). Within the αββ steranes,



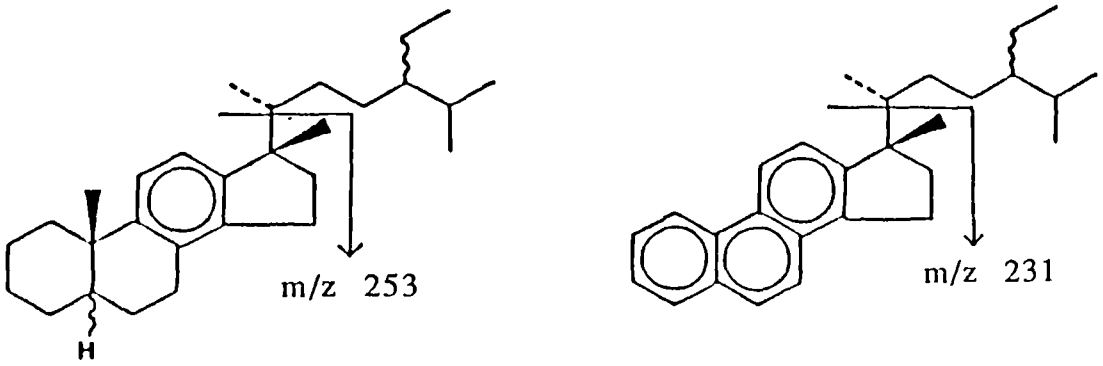
a 5α(H),14α(H),17α(H) steranes



b 5α(H),14β(H),17β(H) steranes



c 13β(H),17α(H) rearranged steranes (diasteranes)



d C-ring monoaromatic steroid

e ABC-ring triaromatic steroid

Fig.3.5 Fragmentation of steroidal hydrocarbons.

an intense fragment is also produced at m/z 218 (Fig.3.5b), which assists in the elucidation of these components. Rearranged steranes (diasteranes) give an intense fragment ion at m/z 259, corresponding to the loss of the side chain (Fig.3.5c).

In immature samples, the presence of βαα steranes is a hindrance because they coelute with αββ compounds under the gc-ms conditions described in the previous section. If the presence of the βαα components was suspected, confirmation was achieved by scanning across the composite peak and monitoring the change in intensity of the ions m/z 149 and 151. The 5β steranes show m/z 151>149 whilst the 5α isomers possess m/z 149>151 (Tokes and Amos 1972). A few samples were run on a DB-17 (30 x 0.25mm i.d.) column which enabled the resolution of βαα from αββ steranes.

The presence of 4-methyl steranes was checked by monitoring m/z 231, corresponding to the additional mass of a methyl group in the A ring.

Mono- and triaromatic steroids gave major fragment ions at m/z 253 and m/z 231 respectively, resulting from the loss of the side chain (Figs 3.5d and 3.5e). The presence of C-ring monoaromatics with methyl groups at the 1 or 4 positions (Section 2.3.3.4.2) can be established by examining the distribution of m/z 245 ions.

3.3.7.3 Aromatic Hydrocarbons

The mass spectra of aromatic hydrocarbons are relatively simple by virtue of their highly condensed ring systems. Unsubstituted polyaromatic hydrocarbons (PAH) possess the simplest mass spectra, displaying an intense ion peak due to the molecular ion (M^+) and smaller peaks (0-50% of M^+) due to the loss of one to four hydrogen atoms. In addition to the M^+ ions, alkylated PAH can be recognised by the production of $(M-15)^+$, $(M-29)^+$ etc ions corresponding to the loss of alkyl side groups.

The simplicity of the mass spectra means that individual isomers of aromatic compounds can rarely be distinguished on the basis of mass spectral evidence alone. Even structurally dissimilar isomers, e.g. fluoranthene and pyrene, can have identical mass spectra. Much reliance was therefore placed on the use of relative retention times and the comparison of mass chromatograms and total ion current (TIC) traces with the published data of Lee *et al.* (1976a, b, 1981), Chaffee and Johns (1983) and Philp (1985a).

A summary of the diagnostic fragment ions used to identify the major compound classes and compounds investigated in this project is given in Table 3.3.

3.3.8 Rock-Eval Analysis

Selected samples were sent to Britoil and Norsk Hydro for Rock-Eval analysis using a Rock-Eval III machine ("Oil Show Analyser").

Table 3.3 Characteristic fragment ions for the principal compound classes / compounds investigated.

Structural Group		Compound Class/ Compound	Characteristic Fragment Ion (m/z)
TERPANES	SATURATED	Bicyclics	123
		Demethylated Hopanes	177
		Tricyclics, Tetracyclics, Hopanes	191
		Methylhopanes	205
STEROIDS	SATURATED	Regular Steranes	217
		αββ Steranes	218
		4-Methyl Steranes	231
		Diasteranes	259
	AROMATIC	Triaromatics	231
		1- or 4-Methyltriaromatics	245
		Monoaromatics	253
AROMATICS	MAINLY DIAGENETIC	Alkylbenzenes	105/119
		Naphthalene	128
		Methylnaphthalenes	142
		Dimethylnaphthalenes	156
		Trimethylnaphthalenes	170
		Phenanthrene/Anthracene	178
		Methylphenanthrenes/Anthracenes	192
		Dimethylphenanthrenes	206
		Trimethylphenanthrenes	220
	MAINLY COMBUSTION-/ PYROLYTICALLY DERIVED	Fluoranthene/Pyrene	202
		Benzofluorenes/ Methylfluoranthenes or Pyrenes	216
		Benzo(ghi)fluoranthene	226
		Benz(a)anthracene/Chrysene/ Triphenylene	228
		Dimethylfluoranthenes or Pyrenes [a]	230
		Methylchrysenes/ Methylbenz(a)anthracenes	242
		Trimethylfluoranthenes or Pyrenes [b]	244
		Benzofluoranthenes/ Benzopyrenes/Perylene	252
		Dimethylchrysenes/ Dimethylbenz(a)anthracenes [a]	256

[a] could also be ethyl

[b] could also be ethylmethyl or propyl

The Rock-Eval analyser was developed by Espitalie *et al.* (1977) as a rapid and relatively inexpensive screening tool designed to determine the source-rock potential of sediments. The powdered rock (c.100mg) undergoes temperature-programmed pyrolysis in an inert atmosphere. Three phases of hydrocarbon evolution are monitored by a flame ionisation detector (FID). The peak designations and the temperature intervals over which they are evolved are shown schematically in Fig.3.6.

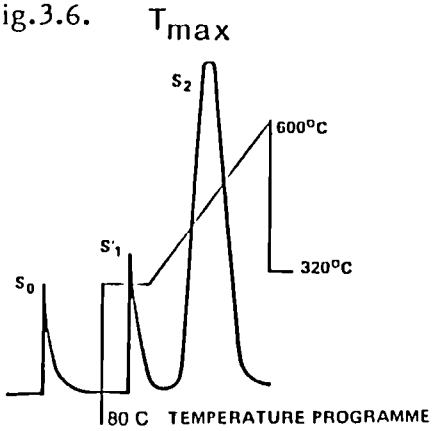


Fig.3.6 Schematic representation of peaks generated by Rock-Eval pyrolysis.

The definitions of the peaks and the parameters associated with them are as follows:-

S_0 measures the free, light hydrocarbons (gases) present in cuttings or core samples. These are evolved up to 80°C.

S'_1 measures the free hydrocarbons (bitumen) in a sample, i.e. the liquid hydrocarbons already generated by the rock. These are evolved over the range 80°C-320°C.

S_2 measures the remaining petroleum-generating potential of the kerogen, i.e. the hydrocarbons evolved when the kerogen is thermally degraded over the range 320°C-360°C.

Tmax is the temperature at which the rate of hydrocarbon evolution reaches a maximum (apex of S_2 peak).

An additional peak, S_4, is also recorded in the analysis and measures the carbon dioxide evolved by the combustion of residual carbon at 590°C, which is used in the calculation of total organic carbon (TOC).

Various source and maturation parameters can be computed from the above measurements. All the samples submitted for Rock-Eval analysis were uncanned core or field samples in which gaseous hydrocarbons were absent. No S_0 peak was therefore observed, and this is disregarded in the calculation of the indices outlined below.

(i) **Hydrogen Index (HI)** is equivalent to mg of S_2 per gram TOC. Service company guidelines on the variation in this parameter with organic-matter type and maturity are presented in Table 3.4.

Table 3.4 Classification of organic matter and hydrocarbon products using hydrogen index.

HI Immature (<0.50%VR)	HI Mature (0.80-1.00%VR)	Kerogen Type	Hydrocarbon Type
>700	200 - 250	I	Paraffinic Oil
350 - 700	200 - 250	II	Oil
200 - 350	100 - 150	II/III	Oil/Gas
100 - 200	50 - 150	III	Gas/Heavy Oil
0 - 100	<50	IV	No Potential

(ii) S_2 (milligrams of hydrocarbon per gram rock) can be used to measure the petroleum-generating capacity of rocks that are immature or in the early stages of catagenesis, but cannot alone distinguish between oil- and gas-generating capacity. The yield of hydrocarbons from pyrolysis can be used as a measure of source-rock capacity employing the scale in Table 3.5.

Table 3.5 Source-rock classification based on S_2 yield.

S_2 (mgHC/g rock)	Potential
< 2	Poor
2 - 5	Fair
5 - 20	Good
> 20	Excellent

(iii) $S_1 + S_2$ is the "genetic potential" (GP) of the rock and represents the total amount of hydrocarbons that the kerogen is able to generate. The following classification has been suggested by Tissot and Welte (1984; Table 3.6).

Table 3.6 Source-rock classification based on genetic potential.

Genetic Potential	Source Potential
$<2kgt^{-1}$ (2000ppm)	no oil source rock, some gas potential
$2 - 6kgt^{-1}$ (2000-6000ppm)	moderate source rock
$>6kgt^{-1}$ (6000ppm)	good source rock

(iv) **Tmax** increases with increasing sample maturity according to the generalised scheme shown in Table 3.7

Table 3.7 Variation in Tmax with maturation level.

Tmax	Maturity Level
<430 - 435	Immature
435 - 465	Oil Window
>465	Gas Window

The values quoted are for type III kerogens: Tmax values are higher for a given rank in type I and II kerogens, in which the greater proportion of carbon-carbon bonds requires more thermal energy for their cleavage. Plots of Tmax *vs* HI are often used to convey the same information as a van Krevelen diagram, i.e. variation in organic-matter type and degree of thermal evolution.

(v) S_1/S_1+S_2 is the "production index" (PI) or "transformation ratio". It is the ratio of the hydrocarbons already formed from the kerogen to the total amount of hydrocarbons that it is capable of generating. This parameter increases with increasing sample maturity. Abnormally high values of the production index indicate the presence of migrated hydrocarbons.

3.3.9 Kerogen Isolation

Kerogen isolation was performed according to the scheme shown in Table 3.8 which is a modified version of the method used by Forsman and Hunt (1958) and more fully discussed by Fowler (1984).

The initial step involves the removal of carbonate minerals by hydrochloric acid and is followed by digestion of the silicate minerals using hydrofluoric acid. As this, or any other, method has so far failed to accomplish the adequate removal of pyrite, residues containing abundant pyrite were added to zinc chloride solution (1.72g/ml) and the "pure" kerogen was pipetted off. The "cleanness" of the separation was checked by optical examination.

Samples were submitted to British Gas for elemental analysis. Strew mounts were also made for optical examination.

Table 3.8 Isolation of kerogens.

(1) Wet extracted rock powder (30g) with distilled water.
(2) Slowly add concentrated HCl (12M) until effervescence ceases and then add a further volume of HCl (approximately 25% of the original volume).
(3) Stir for 24 hrs at room temperature, then 8 hrs at 50°C.
(4) Remove acid solution and wash (x2) with distilled water.
(5) Add HF (60%) and 20ml (12M) HCl and stir for 24 hrs at 50°C.
(6) Slowly add an excess of a saturated solution of boric acid to neutralise HF and allow mixture to stir for a further $\frac{1}{2}$ hr.
(7) Remove boric acid solution and wash residue (x2) with hot distilled water.
(8) Add dilute HCl (4M) and stir for 24 hrs at 50°C.
(9) Remove acid solution and wash with distilled water.
(10) Add saturated ammonium carbonate to the residue, centrifuge and decant the supernatant liquid.
(11) Add hot distilled water to the residue, centrifuge and decant supernatant liquid.
(12) Add hot 4M HCl to residue, centrifuge and decant supernatant.
(13) Add hot distilled water to residue, centrifuge and decant supernatant.
(14) Repeat steps 10-13 twice.
(15) Wash residue with hot distilled water (x4).
(16) Dry kerogen in vacuum oven (28°C).

CHAPTER 4

VARIATION IN ORGANIC-MATTER TYPE

4.1 INTRODUCTION

The aim of this chapter is to present an integrated organic petrological and geochemical evaluation of the different types of sedimentary organic matter occurring within the Carboniferous succession of the eastern and central Midland Valley. All sample descriptions are given in Appendix I. The petrological descriptions of the samples used for geochemical analysis are presented separately (Table A.1) for ease of reference.

4.2 ORGANIC PETROLOGY

The organic content of argillaceous sediments in the Midland Valley is generally high. The "average" argillaceous sediment is a silty shale or siltstone in which the organic matter is dominated by macerals derived from vascular plants. The maceral assemblage usually comprises at least 60% inertinite, up to 20% vitrinite and 10-20% liptinite, the latter usually represented by sporinite. The extent of matrix (bitumen) staining is invariably light to moderate with some additional bitumen wisps and flecks.

Also common within the study area, and often occurring within only a few feet of the humic-rich lithologies, are sediments containing abundant algal macerals. The major algal components are usually *Botryococcus*-related telalginite and lamellar alginite (lamalginite) which, in the richest samples, give rise to the oil shales torbanite and lamosite respectively. Both the telalginite and lamalginite components may be "diluted" by varying amounts of humic and inorganic matrix material, but they may still be present in sufficient quantities to render the sediment in which they occur an oil shale.

The first section describes the organic petrology of algal-rich sediments in the Midland Valley, considering firstly the characteristics of the lamositic and torbanitic end members of the lacustrine source-rock series found in the area. The petrology of other sediments in which the bulk of the organic assemblage is known or thought to be of algal origin is discussed subsequently. Although many cannel coals and marine bands may contain abundant algal matter, for convenience these deposits are dealt with in separate sections.

4.2.1 Algal-Rich Sediments

4.2.1.1 Lamosites

Sediments falling within this category include many of the Dinantian oil shales of the Lothians which were extensively mined and formed the basis of the Scottish oil-shale industry for over a hundred years. The petrography of these

shales also applies to other, more thinly developed deposits which occur sporadically throughout the Calciferous Sandstone Measures (Strathclyde Group) sequence in Fife and which are of insufficient thickness to be worked commercially.

In hand specimen the shales conform to the description of lamosite given by Cook *et al.* (1981), being fine grained, finely laminated and often very flexible in places. Some shales may adopt a contorted "curly" appearance, long known to miners as indicative of very rich, high oil-yielding deposits (Carruthers *et al.* 1912). The finely-laminated nature of these shales can be discerned in reflected - light where it is best represented by alternating organic-rich and organic-poor layers which impart a distinct banding to the rock. Less well defined is the layering imparted by the parallel or sub-parallel alignment of fine, dark filamentous matter. The extent of overall matrix stain in these sediments varies from light to very dark. More detailed characterisation of the organic matter in lamosites is only possible using fluorescence microscopy. From this mode of analysis, it is apparent that the dominant maceral in the lamosites is lamalginite which, in low-maturity samples, displays a moderate to intense yellow fluorescence. The general appearance is of a mass of anastomosing filaments of varying length which are intimately entwined with the sedimentary matrix which may be highly pyritic and/or calcareous. Depending on the degree of preservation and compaction, individual lamellae (approximately 1µm thick) may be seen. The lamalginite component in Midland Valley lamosites can be resolved into two types, discrete or layered lamalginite (*sensu* Hutton 1987; see p.53). One form invariably predominates in a given sample, but both types may co-exist, usually in the form of separate layers or lenses. Variations in lamosite and lamalginite petrology are illustrated in Plates 4.1 to 4.18. Most of the lamalginite occurs in the form of thin, sinuous filaments which are *c.*20-50µm long and, when resolvable, are *c.*1-2µm thick. They may have well-defined boundaries (Plates 4.2 and 4.5), but are more commonly encountered as diffuse wisps (Plate 4.4). This algal morphology falls within the category of discrete lamalginite. Thicker and longer lenses and layers of lamalginite (*c.*10-50µm thick) may be observed in samples containing abundant discrete lamalginite (Plate 4.4), and, from the analysis of numerous samples, it is likely that these lenses arise through the felting together of the discrete filaments and do not constitute a separate algal type. Samples containing discrete lamalginite correspond to those in which only a crude laminar development is observable in reflected light (Plates 4.1 and 4.3).

In addition to the lamalginite described above, both longer and shorter filaments are found in Midland Valley lamosites. Examples of the shorter type

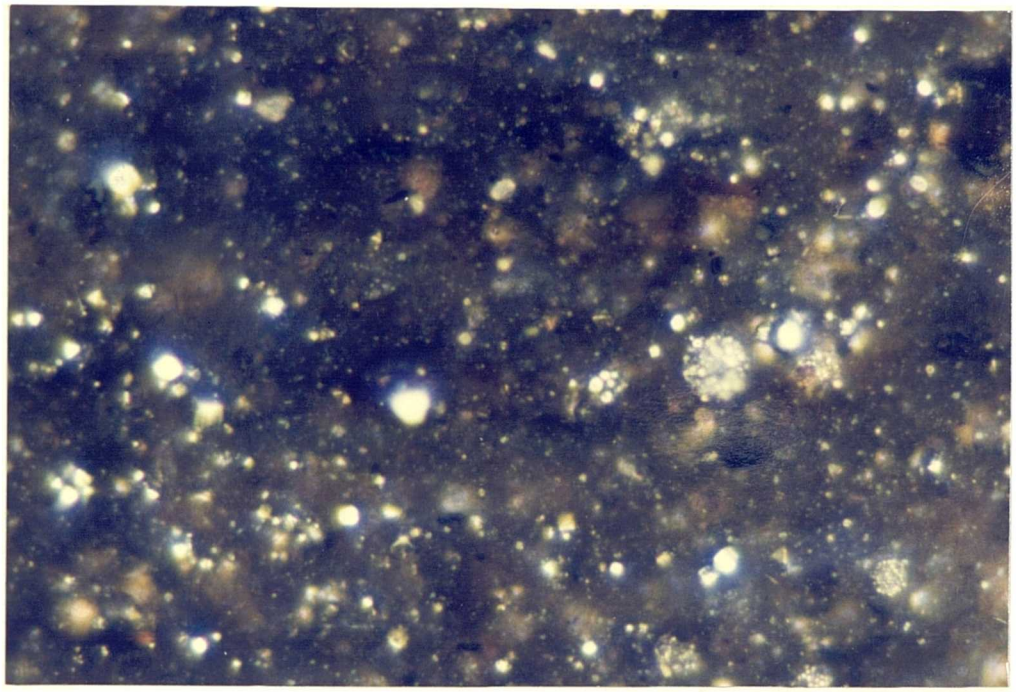


Plate 4.1 Lamosite: reflected light, oil immersion, plane-polarised light.

St.Monance; sample SM 7.

x750

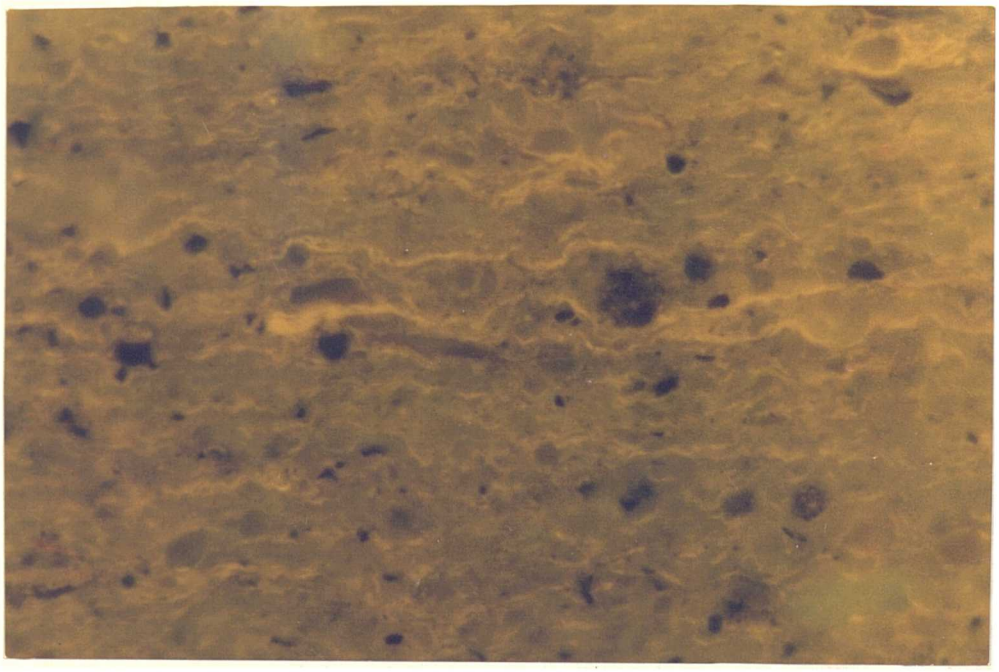


Plate 4.2 Lamosite showing discrete lamalginite filaments; same field of view as above: blue-light excitation, oil immersion.

x750

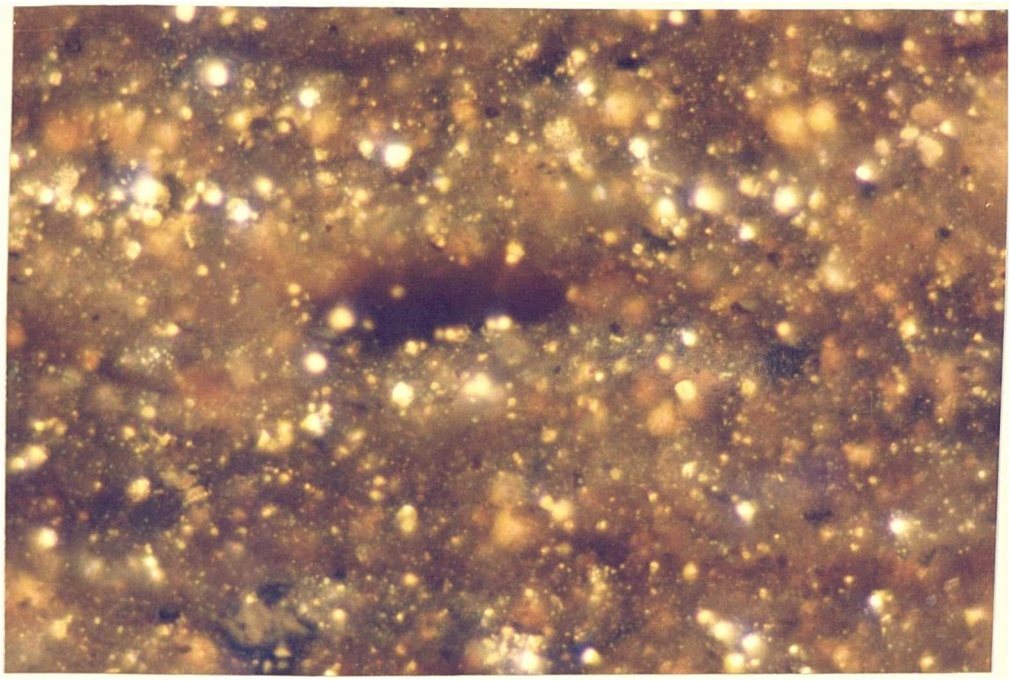


Plate 4.3 Lamosite: reflected light, oil immersion, plane-polarised light.

St.Monance; sample SM 7

x750

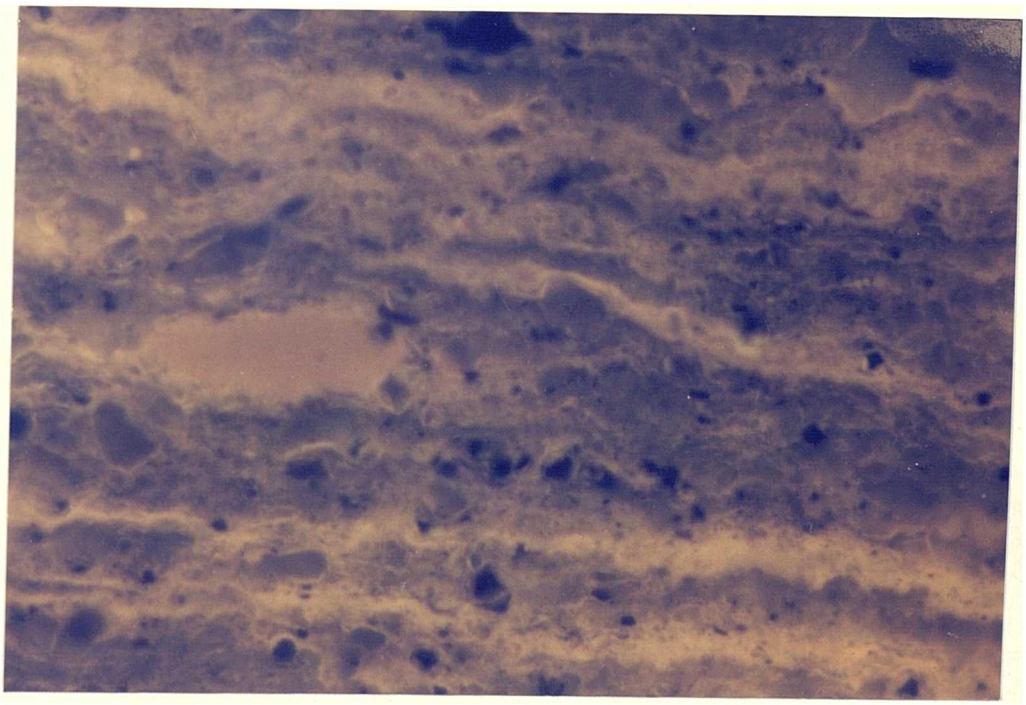


Plate 4.4 Lamosite showing aggregation of discrete lamalginite filaments; approx. same field of view as above: blue-light excitation, oil immersion.

x750

Plate 4.5 Lamosite showing long, discrete algal filaments: blue-light excitation, oil immersion.

Dunnet Shale, Burntisland; sample DS.

x750

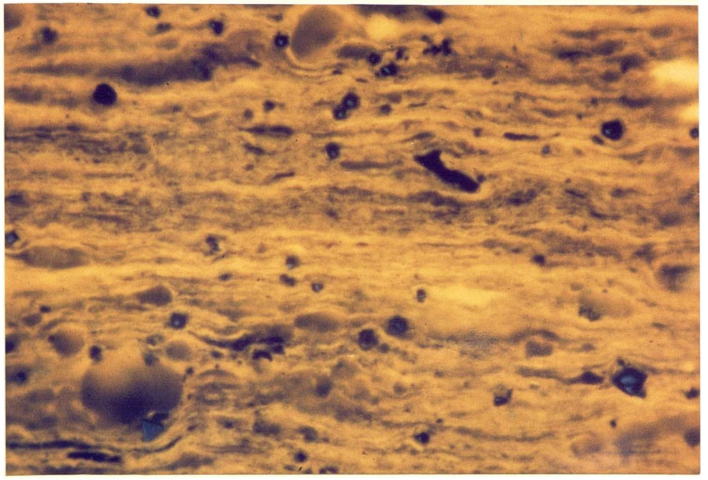


Plate 4.6 Lamosite: reflected light, oil immersion, plane-polarised light.

Fells Shale, Tarbrax; sample Ca 20.

x750

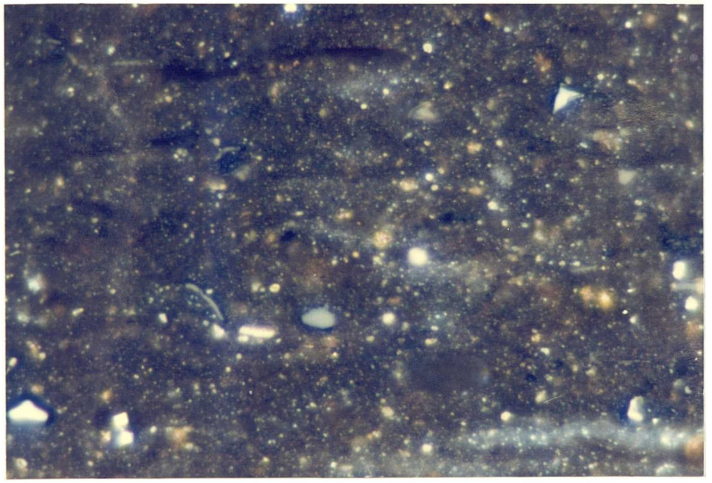
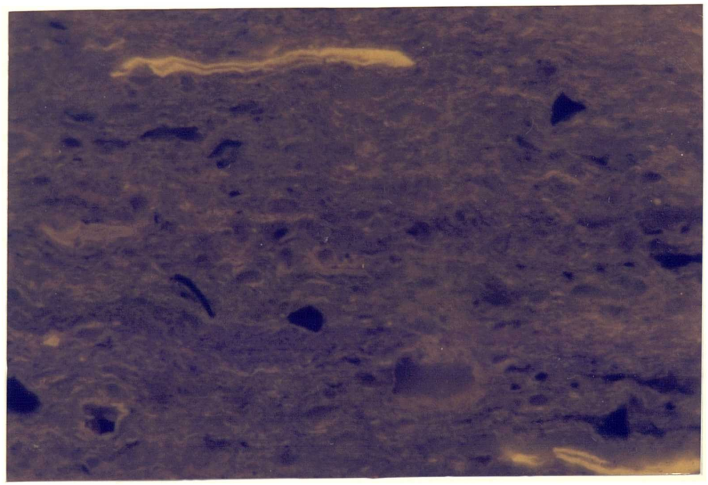


Plate 4.7 Lamosite showing fine, flecky, discrete lamalginite. Elongate double-walled bodies are probably algae: blue-light excitation, oil immersion (same field of view as above).

x750



are shown in Plates 4.6-4.9. The bulk of the algae in the rock matrix is still classed as discrete lamalginite, but its much smaller size (*c.*5-10μm) gives a marked flecked appearance to the groundmass. Any preferred orientation of organic or mineral components in the matrix fabric is more difficult to elucidate in reflected light (Plate 4.6) than in those samples containing the longer algal filaments. Both types of discrete lamalginite referred to above form films around mineral grains and are intimately associated with the sedimentary matrix.

Many samples contain filamentous algal matter which can be traced over much greater distances (several hundreds of microns) than the discrete lamalginite and, in transverse sections, is more continuous along the plane of the bedding (Plates 4.10-4.14). Although many thin algal filaments can be discerned (their boundaries are generally more diffuse than those of discrete lamalginite), much of this longer lamalginite is present in the form of thick algal sheets (*c.*5-50μm) which gives rise to the banded appearance of the samples in reflected (Plate 4.12) and blue light (Plates 4.10, 4.11, 4.13). This type of lamalginite conforms to the description of layered, continuous or band lamalginite (Sherwood *et al.* 1984; Hutton 1987). The anastomosing habit of this continuous lamalginite and the manner in which it is cryptically intermixed with the clay matrix are more pronounced than in samples containing abundant discrete lamalginite, and in many areas the algal matter forms a matrix in which the mineral grains lie. Furthermore, the degree of preservation of the band lamalginite is far more variable than in the discrete variety: it often takes on the form of an amorphous, moderate- to intensely-fluorescing, yellow, gelatinous ooze (Plate 4.14). Both discrete and layered lamalginite may drape around mineral and fossil fragments and, in some cases, the laminae display slump structures, all features indicative of soft-sediment deformation.

Attempts to identify the precursors of the algal types described above proved fruitless. This problem stemmed from the failure of the kerogen-isolation procedure to separate the lamalginite from the mineral matrix, thus proving the extremely intimate nature of the association between the organic and inorganic matter in lamosites. Mounting the kerogen on strew slides and viewing in transmitted light also failed to resolve any morphological features which could have aided identification.

Inferences about the type and origin of the lamellar organic matter contributing to the Lothians-type lamosites were made by comparing their petrological characteristics with those from lamosites occurring in other parts of the world in which lamalginite of similar appearance has been described and the precursors reasonably well defined. Discrete lamalginite of the type described

Plate 4.8 Lamosite containing fine, flecky, discrete lamalginite and other wispy ?algal structures: blue-light excitation, oil immersion.

Fells Shale, Tarbrax; sample Ca 20.

x750

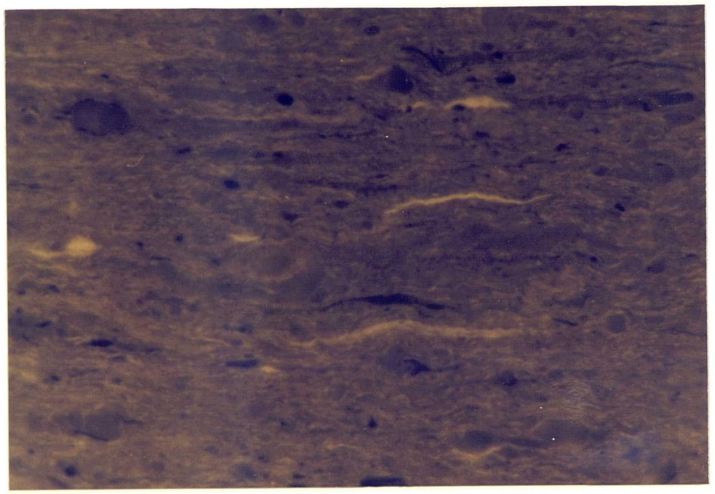


Plate 4.9 Lamosite containing fine, flecky, discrete lamalginite and other brightly-fluorescing ?algal bodies. Thin-walled spores discernible in centre: blue-light excitation, oil immersion.

Broxburn Shale, Mid Calder; sample BROX.

x750

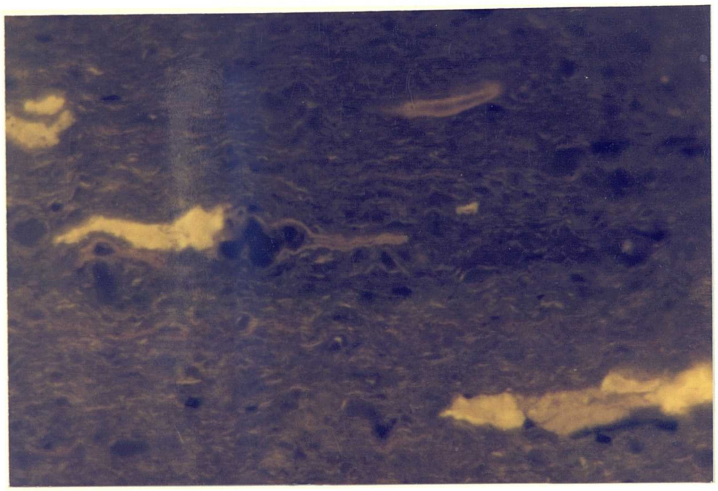


Plate 4.10 Low-magnification photomicrograph of lamosite containing layered (continuous or band) lamalginite. Note diffuse nature of bands: blue-light excitation, oil immersion.

Dunnet Shale, The Craigs, South Queensferry; sample QF E.

x300

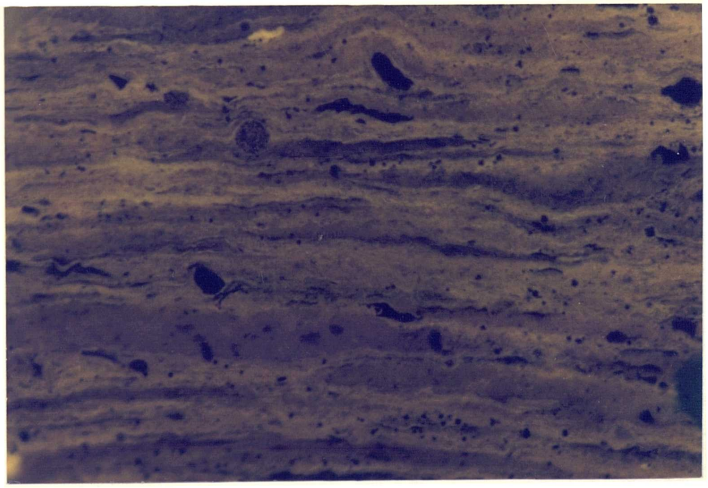


Plate 4.11 High-magnification photomicrograph of lamosite shown in Plate 4.10.

x750

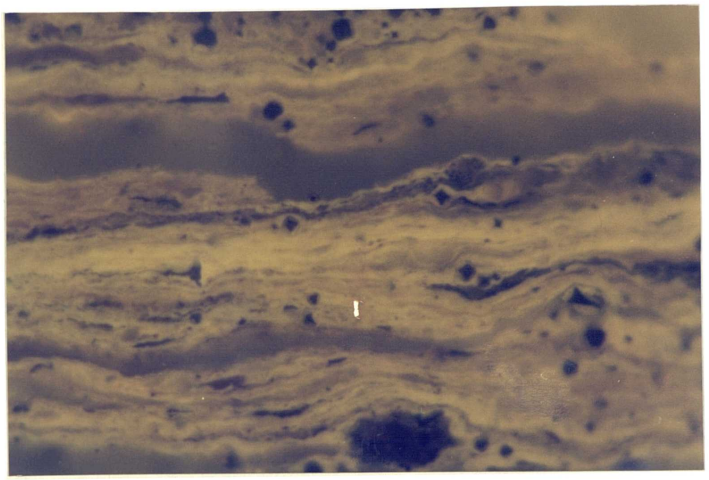


Plate 4.12 Banded appearance of lamosite: reflected light, oil immersion, plane-polarised light.

Dunnet Shale, The Craigs, South Queensferry; sample QF E.

x750

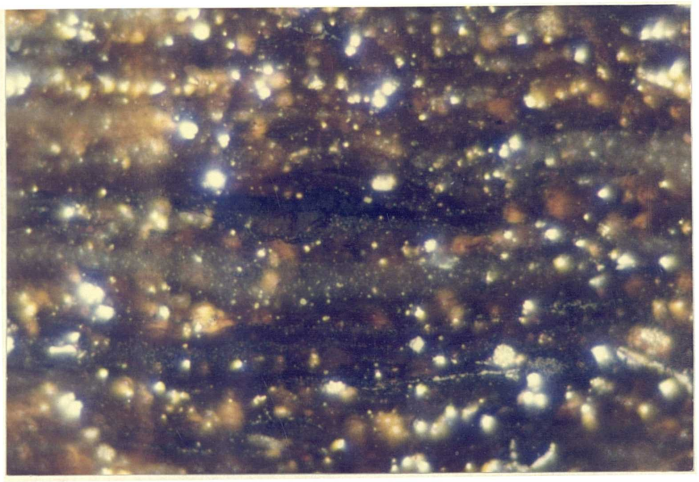
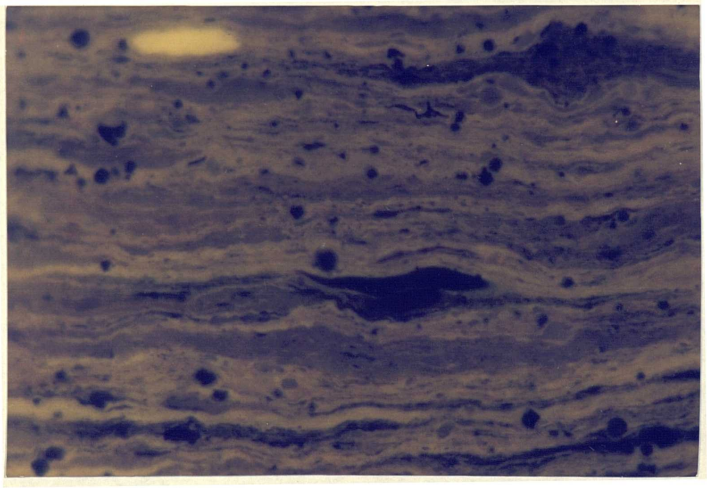


Plate 4.13 Same field of view as above: blue-light excitation, oil immersion.

x750



above has been recognised as the dominant organic component in Tertiary lamosites of the Rundle and Condor type from Queensland (Hutton *et al.* 1980; Cook *et al.* 1981). In these samples, the discrete lamalginite is considered to be largely the remains of the planktonic Chlorophycean alga *Pediastrum*. Other precursors giving rise to discrete lamalginite have also been described in Australian lamosites, and these are also thought to be derived from planktonic green algae. Thus, although the botanical affinities of the discrete lamalginite occurring in Midland Valley lamosites could not be specifically ascribed to *Pediastrum*, the morphology and mode of occurrence of the discrete algal filaments are suggestive of a planktonic, probably green-algal precursor.

The layered lamalginite in Midland Valley lamosites displays features analogous to those described in the Green River Shale and other deposits where the precursor organisms are believed to be benthonic, mat-forming, blue-green algae (Hutton *et al.* 1980; Cook *et al.* 1981; Sherwood *et al.* 1984). A similar origin may therefore be feasible for the layered lamalginite described from the Scottish lamosites. The variation in lamalginite morphology has important implications for the interpretation of depositional environments and is discussed, in conjunction with geochemical data, in Section 4.4.

In addition to the lamalginite components described above, which form the bulk of the organic matter in the Scottish lamosites, other lamellar algae may also be found. These algae occur as more intensely-fluorescing wisps (Plate 4.8) or as thicker, double-walled structures which probably represent compressed, spherical cysts (Plate 4.7).

Minor quantities of *Botryococcus* telalginite are invariably associated with the lamosites, although the internal structures are not generally as well preserved as those in *Botryococcus* colonies within torbanites, a feature first recognised by Conacher (1917: see also Plates 4.5 and 4.13). Other elongate bodies are found within lamosites (Plate 4.9) and, from their high fluorescence intensity, are probably of algal (telalginite) origin.

Besides the algal matter, the Scottish lamosites may contain terrestrial debris; vitrinite and sporinite are usually present in very small amounts whilst inertinite fragments are more abundant. Moderate to dull-fluorescing orange bitumen and/or intense yellow-fluorescing hydrocarbon material are not uncommonly found within the cavities of inertinite macerals (Plates 4.15 and 4.16). Other microscopically-discernible components often found in the lamosites are fish remains, for example bones, spines and scales as well as ostracod shells and coprolites.

Plate 4.14 Degraded layered (continuous or band) lamalginite draping around mineral grain and other amorphous, ooze-like algal matter: blue-light excitation, oil immersion.

Dunnet Shale, The Craigs, South Queensferry; sample QF E.

x750

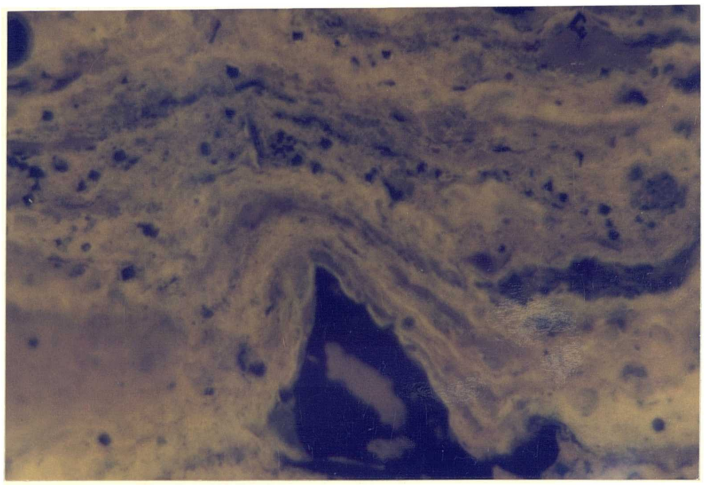


Plate 4.15 Fusinite fragment in lamosite: reflected light, oil immersion, plane-polarised light.

Dunnet Shale, Whinnyhall mine adit, Burntisland; sample DS.

x750

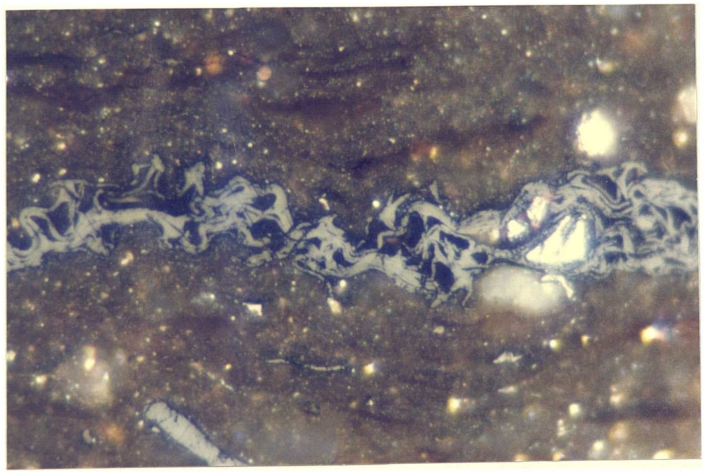
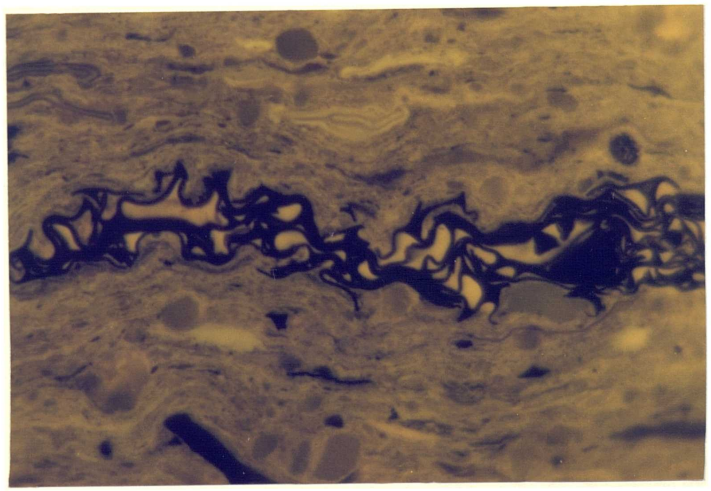


Plate 4.16 Same field of view as above showing bitumen in fusinite cavities: blue-light excitation, oil immersion.

x750



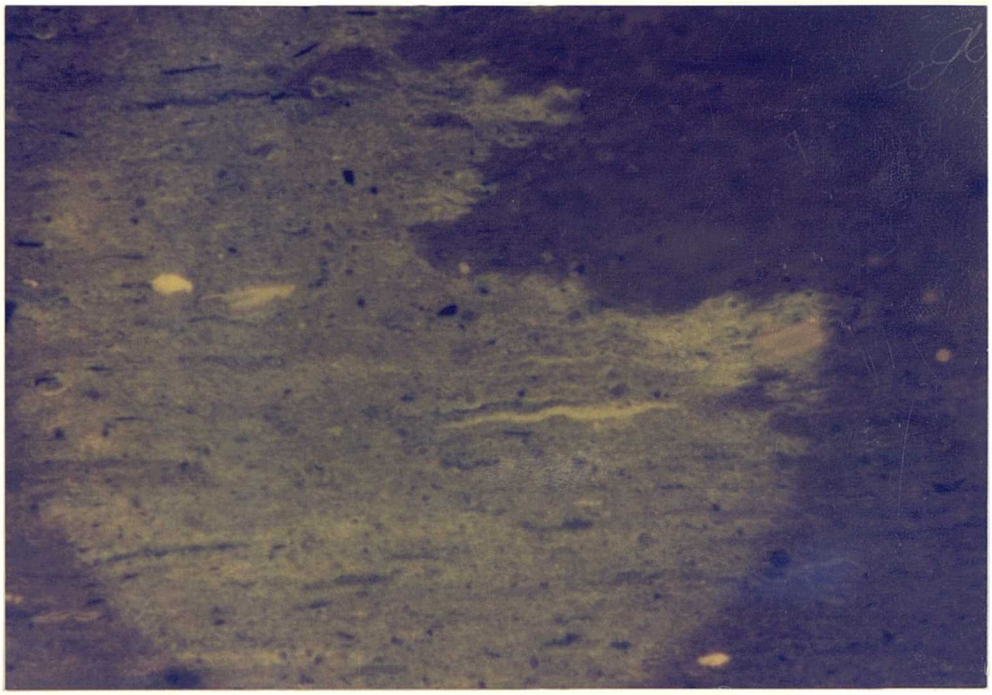


Plate 4.17 Low-magnification photomicrograph showing positive fluorescence alteration of lamosite groundmass: blue-light excitation, oil immersion.

Fells Shale, Tarbrax; sample Ca 20.

x300

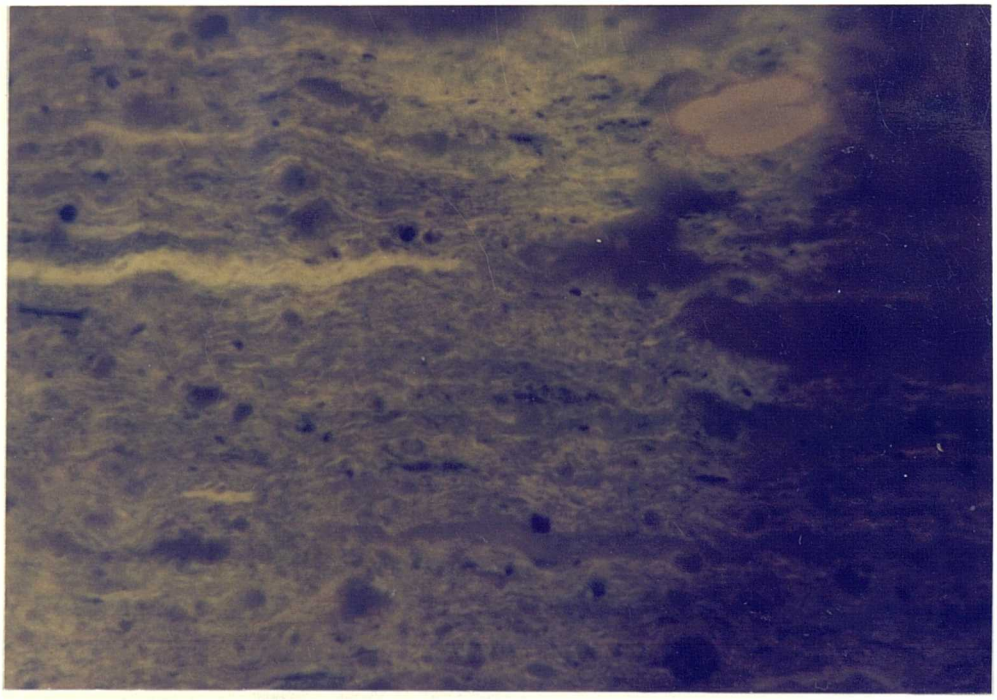


Plate 4.18 Detail of the above. Note that the groundmass is now seen to contain abundant discrete lamalginite which was not readily resolvable in Plate 4.17: blue-light excitation, oil immersion.

x750

A further characteristic feature of Midland Valley lamosites (and many other liptinite-rich sediments from the area) is the background fluorescence which emanates from the mineral matrix. After irradiation for 10-20 minutes, the fluorescence undergoes strong positive alteration which often enhances the morphology of liptinitic macerals (Plates 4.17 and 4.18). This background fluorescence is embodied in the terms "mineral-bituminous groundmass" Teichmüller and Ottenjann 1977; Teichmüller 1987) and "matrix fluorescence" (Robert 1979). The fluorescence may originate from liptinitic material present below the surface of the sample, finely comminuted or sub-microscopic lipoid matter or dispersed hydrocarbon material.

Plates 4.17 and 4.18 also illustrate the importance of using high-power objectives and performing sample descriptions after irradiation of the sample for several minutes. This practice allows the recognition of small, discrete liptinitic components which would otherwise go unnoticed. For example, the groundmass observed under fluorescence using a low-power objective (Plate 4.17) appears fairly homogenous both before and after long-term irradiation. After prolonged exposure to blue-light excitation and using a high-powered objective (Plate 4.18), much of the fluorescence in this sample can be attributed to very fine, discrete lamalginite wisps which were not readily apparent in Plate 4.17.

4.2.1.2 Torbanite and Torbanitic Shales

The term "torbanite" in this thesis (see p.52) is reserved for sediments containing at least 90% *Botryococcus* telalginite, thus corresponding with the petrographic characteristics of the type deposit from Torbanehill (pictured in Skilling 1938). In this classic deposit, the *Botryococcus* content is so high that the individual colonies are separated by only a thin veneer of sediment. Although *Botryococcus* is the commonest form of telaginite occurring with the Carboniferous succession of the Midland Valley, major accumulations of these algae in the form of torbanites are rare. "Torbanitic shales", a term used in this project to describe shales containing $\geq$50%, but <90% (vol) *Botryococcus* telalginite, are more common. Any sediment containing $\geq$20% *Botryococcus* is referred to as *Botryococcus*-rich. The petrological characteristics of several samples containing major quantities of *Botryococcus* are shown in Plates 4.19-4.29. The best known of these samples are the Westfield Oil Shale (Plates 4.20 and 4.21) and the Westfield Canneloid Shale, both of which were formerly worked as sources of shale oil from Passage Group strata in the Westfield Basin. The Westfield Oil Shale and Canneloid Shale are not torbanites, as is often thought, but fall more appropriately within the classification of torbanitic shales on the basis of their

Plate 4.19 Torbanite with central *Botryococcus* colony displaying virtually no fluorescence: blue-light excitation, oil immersion.

Eskmouth 50/56 borehole, Fife-Midlothian Basin; sample ESC.

x300

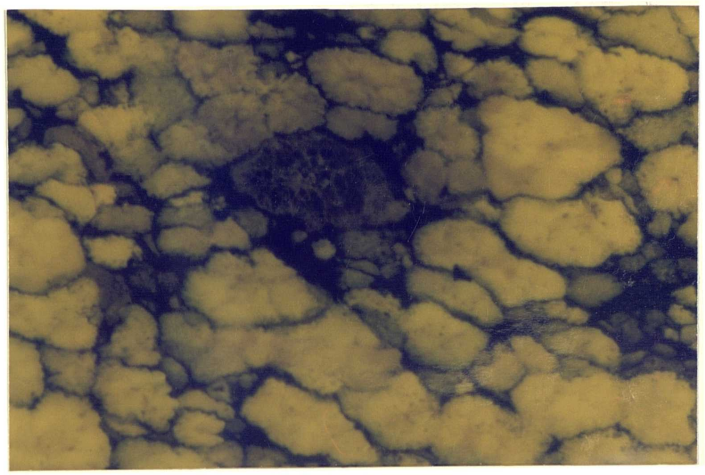


Plate 4.20 Westfield Oil Shale (torbanitic shale) showing *Botryococcus* telalginite with poorly defined internal morphology and variable fluorescence colours and intensities. Circular spore fragment occurs towards top left of photomicrograph: blue-light excitation, oil immersion.

Borehole 1998, Westfield Basin; sample WDOS.

x750

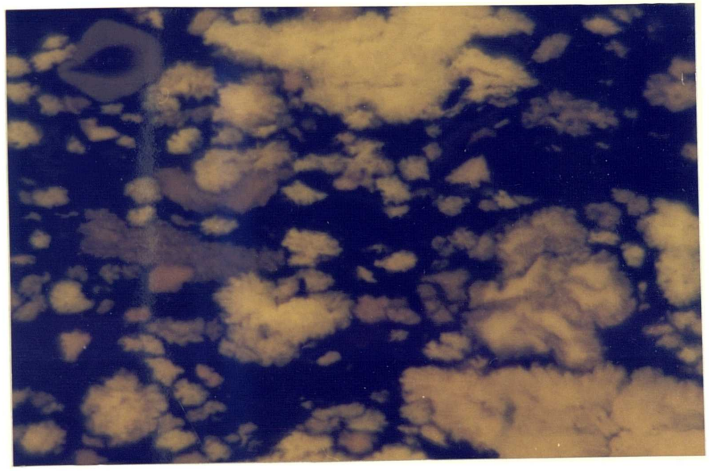
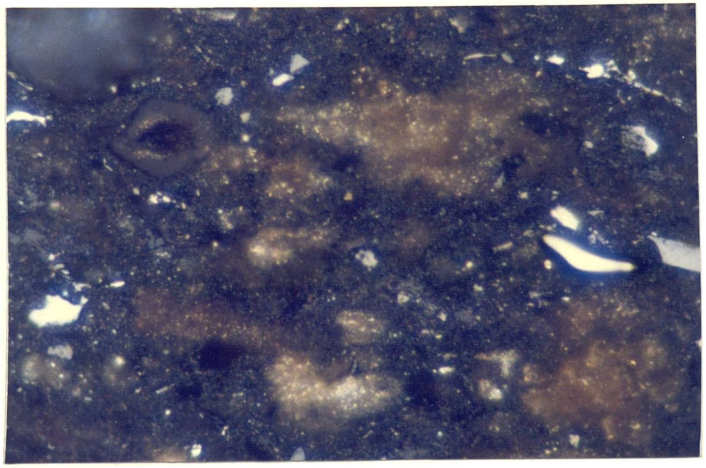


Plate 4.21 Approximately same field of view as above: reflected light, oil immersion, plane-polarised light.

x750



Botryococcus content (52% and 61% respectively). Some parts of the above samples may, however, contain closely-packed *Botryococcus* colonies, thus becoming torbanitic in places. The only "true" torbanite encountered throughout the course of the whole study was from the Eskmouth No.50 Borehole, in the Midlothian Basin (Plate 4.19), overlying the Extra Coal (Passage Group). This sample is hereafter referred to as the "Eskmouth torbanite".

All the *Botryococcus* telalginite observed within the sediments in the Midland Valley was of the *Pila* form, although Blackburn and Temperley (1936) did record *Reinschia* colonies in the Torbanehill torbanite. The *Pila* bodies in Midland Valley samples are elliptical or rounded in shape, usually 30-40µm in diameter, and possess "fluffy" or crenulated margins. In low-rank samples, the colonies display a strong, yellow or orange-yellow fluorescence. In some samples, the fluorescence colours and intensities can vary between different colonies as well as within the same colony (Plate 4.20). Some telalginite bodies may barely fluoresce at all, despite being within samples containing abundant brightly-fluorescing algal matter (Plate 4.19). Any variation in the optical properties of *Botryococcus* which is discernible under blue-light excitation is not apparent under reflected-light examination, although the non-fluorescing algal bodies (Plate 4.19) are nearly always seen, in reflected light, to be encrusted or completely pseudomorphed by pyrite.

Most of the *Botryococcus* telalginite encountered in the Midland Valley retains relatively little of the internal cellular structure observed in the living colonies. A notable exception occurs in the Canneloid Shale of the Westfield Basin. Lying only 70m above the Westfield Shale, within the same coal-bearing sequence known as the Boglochty Beds, the degree of preservation of *Botryococcus* in the Canneloid Shale is much greater than that observed in the algal colonies of the Westfield Shale; indeed the algae in the former deposit represent the best-preserved *Botryococcus* recorded throughout the present project. Not only is the sample unusual in that the whole colonial structure of the algae is preserved (generally *c.*100µm in diameter), the algae have also retained their internal, tubular morphology (Plate 4.22) as well as the individual, fine peripheral thecal structures with their surrounding delicate fringe of tissue (Plate 4.23). The enhanced state of preservation of *Botryococcus* in the Canneloid Shale is also pronounced in reflected light (compare Plate 4.21 with Plate 4.26). In addition to the large, exquisitely preserved colonies which are surrounded by comminuted *Botryococcus* fragments, the Canneloid Shale is unusual in that the telalginite can be resolved into two types based on differences in the internal cellular morphology. The algal bodies in the centre of Plate 4.24 are not only

Plate 4.22 Torbanitic area in the Canneloid Shale showing whole colonial structures of *Botryococcus*, with finely-preserved cellular structures, surrounded by fragments: blue-light excitation, oil immersion.

Borehole 1990, Westfield Basin; sample WDCS.

x300

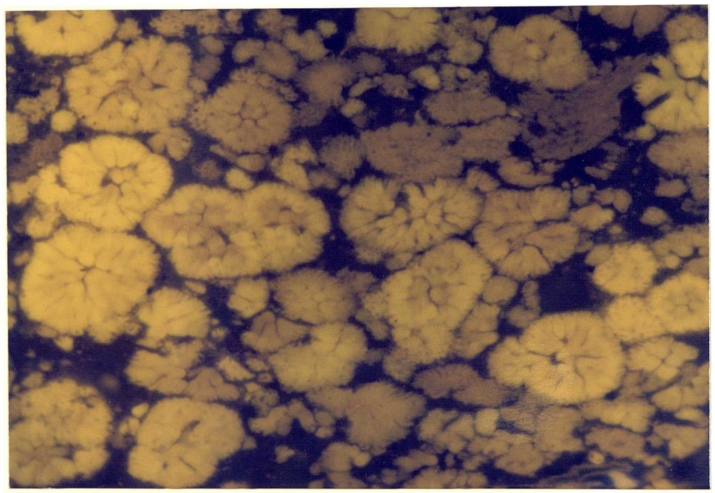


Plate 4.23 Thecal detail of *Botryococcus* colony in the Canneloid Shale: blue-light excitation, oil immersion, slightly overexposed.

Borehole 1990, Westfield Basin; sample WDCS.

x750

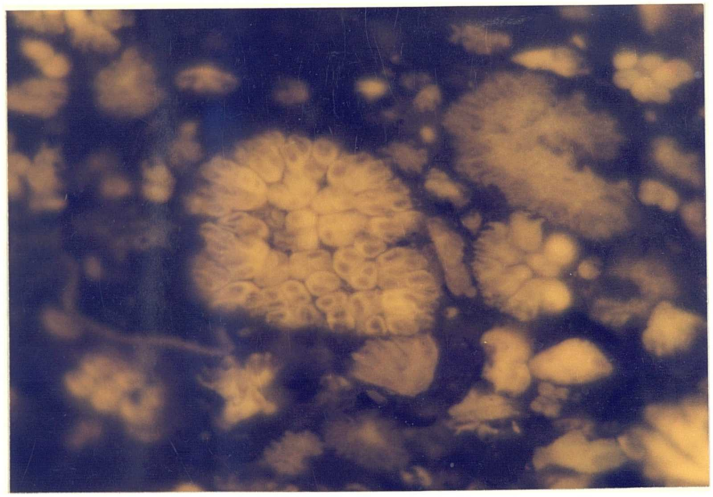


Plate 4.24 Large *Botryococcus* colonies in Canneloid Shale showing brown fluo rescing rims and simple internal branching: blue-light excitation oil immersion.

Borehole 1990, Westfield Basin; sample WDCS.

x300

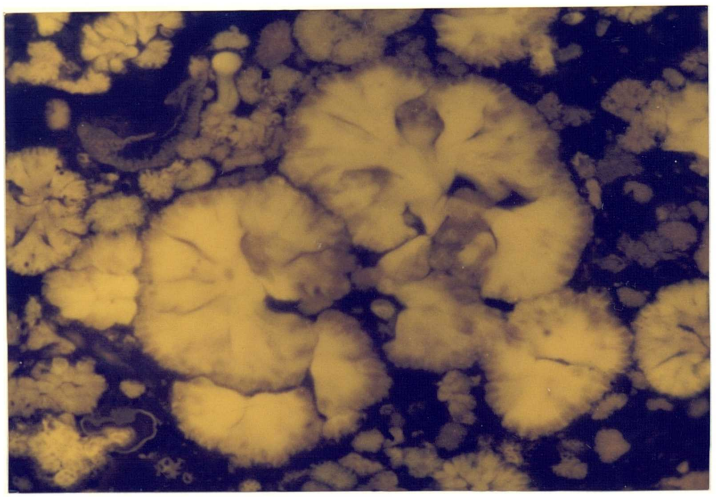


Plate 4.25 Fragment of large *Botryococcus* colony surrounded by "normal"-sized colonies: blue-light excitation, oil immersion.

Canneloid Shale, Bogside 2 borehole, Westfield Basin; sample BEB 4045.

x300

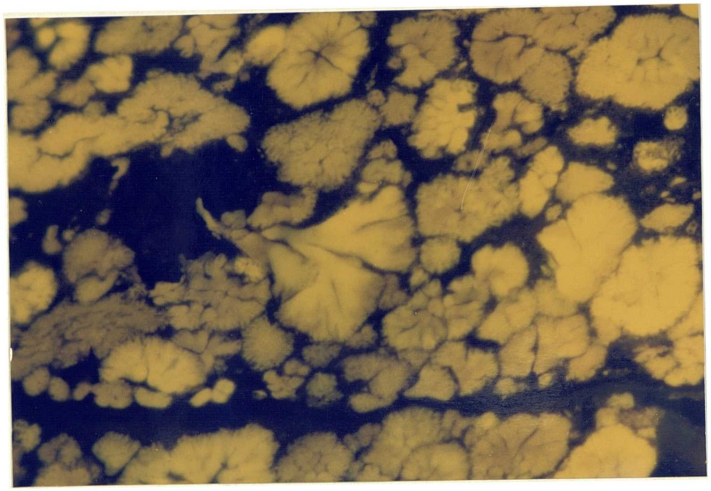


Plate 4.26 Vitrinite-like stringer with complete *Botryococcus* colony and other fragments: reflected light, oil immersion, plane-polarised light.

Canneloid Shale, borehole 1990, Westfield Basin; sample WDCS.

x750

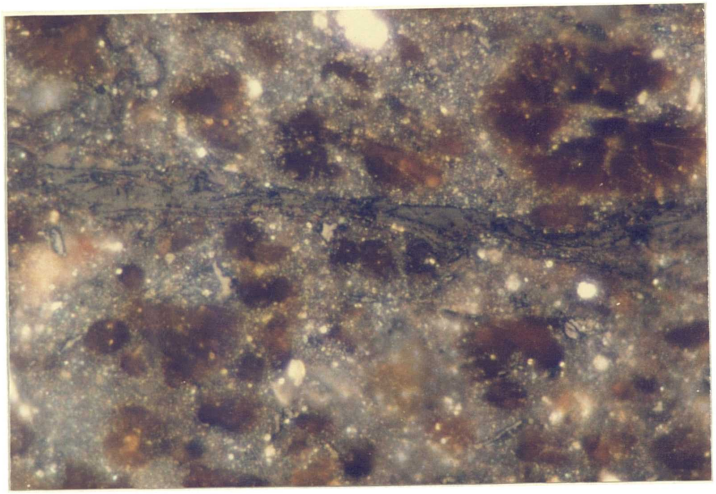
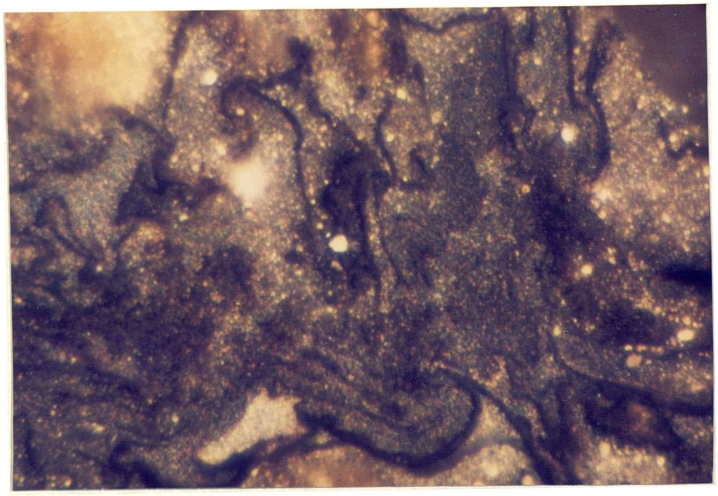


Plate 4.27 Thin, ramifying, vitrinite-like material exuding brown bituminous matter: reflected light, oil immersion, plane-polarised light.

Westfield Oil Shale, borehole 1998, Westfield Basin; sample WDOS.

x750



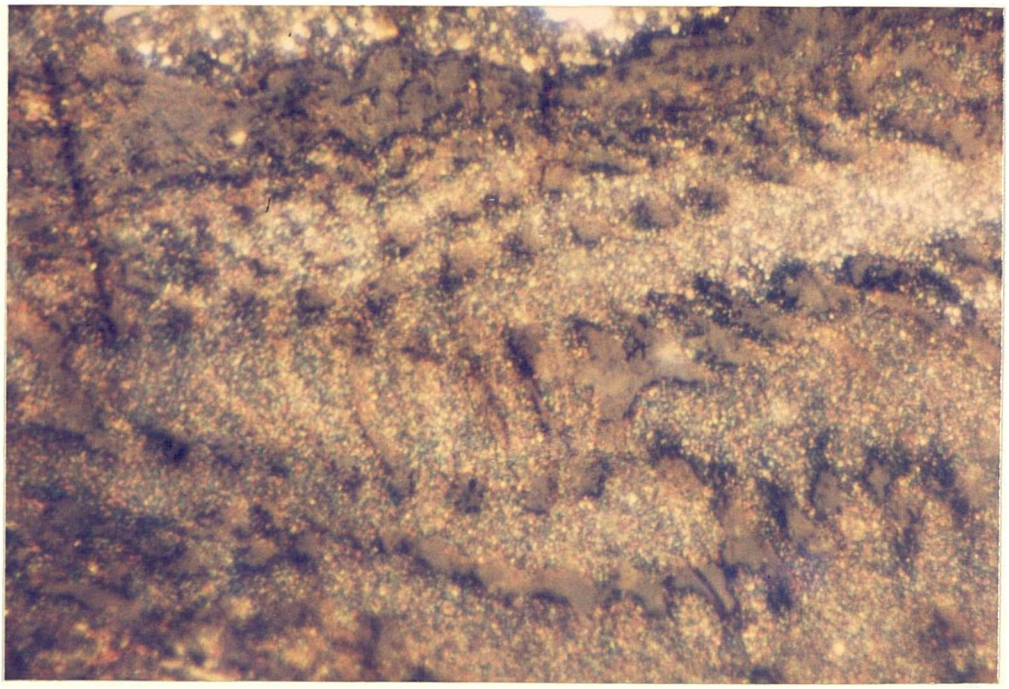


Plate 4.28 Vitrinite-like stringers with associated cell structures containing abundant micrinite: reflected light, oil immersion, plane-polarised light.

Westfield Oil Shale, borehole 1998, Westfield Basin; sample WDOS.

x750

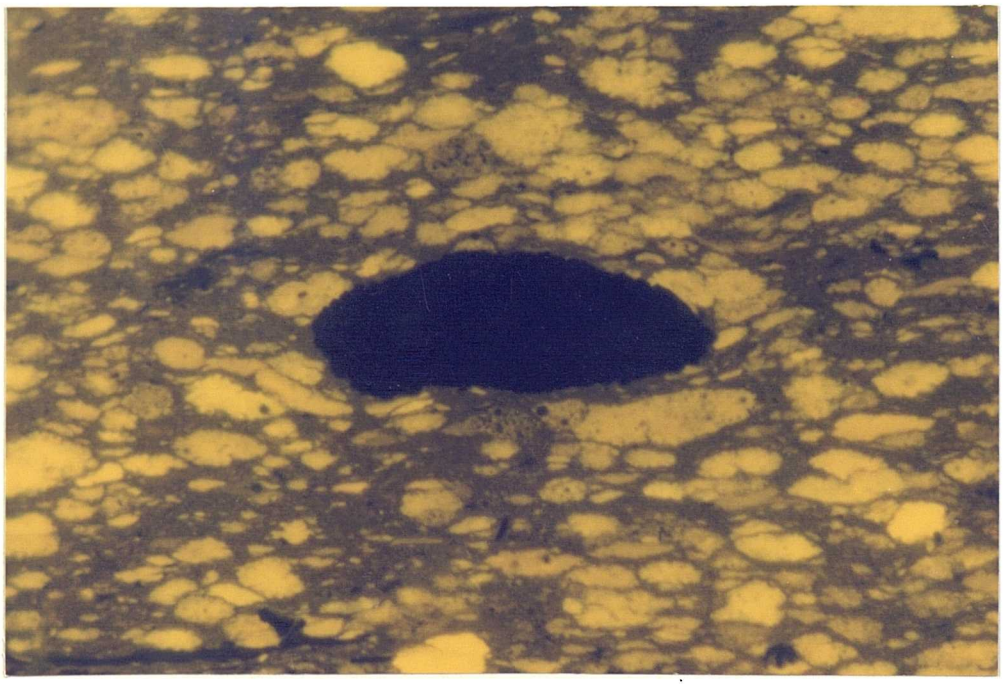


Plate 4.29 Coprolite in torbanitic shale: blue-light excitation, oil immersion.

Lillies Shale; sample Ca 9.

x300

much larger than the adjacent, more commonly-occurring algae which are large *per se*, they are quite different in appearance because their internal processes are much thicker, which gives rise to a less complex system of branching. These larger colonies are rarely less than 100μm in diameter and can exceed 200μm. Fragments of this type of algal structure can be detected amongst the other types of *Botryococcus* material (Plate 4.25). The larger, structurally-simpler algae in the Canneloid Shale invariably display a dull, brown fluorescence around their peripheries, which contrasts markedly with the moderate to intense yellow fluorescence of the main algal bodies. This feature occasionally occurs in the smaller algae within the Canneloid Shale and also in Westfield Oil Shale, but is not so well defined in the latter.

In addition to the *Botryococcus* colonies, the torbanite and torbanitic shales studied contain material with similar morphological characteristics to the "stringers of low-reflecting, uniform grey material" reported by Allan *et al* (1980) in the Torbanehill torbanite. The material occurs as stringers of varying thickness (Plate 4.26) which can sometimes form an interconnecting network in parts of the sample. These networks are particularly common in the Westfield Oil Shale. This grey material may also pass into fine, ramifying strings from which brown, bituminous material exudes (Plate 4.27), and it can also pass into material showing remnant cell structures which may contain micrinite (Plate 4.28). Besides this vitrinitic material (discussed further in Section 4.4), inertinite fragments invariably contribute to the maceral assemblage in torbanite and torbanitic shales, although inertinite is a minor component, not exceeding 10% of the total organic content of the samples. Minor quantities of spore debris may also occur as can various fish remains, for example spines and coprolites (Plate 4.29).

4.2.1.3 Miscellaneous

Representative photomicrographs illustrating other types of algal associations occurring within Midland Valley sediments are shown in Plates 4.30 to 4.36. Although the sediments discussed in this section have very high organic contents (see Section 4.3.2 for TOC data) and have kerogens consisting mainly of algal matter, or matter thought to be of algal origin, similar associations (apart from that shown in Plates 4.34-4.36) may occur in organically much leaner sediments. In addition to the "average" 30-40μm wide *Botryococcus* telalginite remains that are most commonly found, much smaller fragments are also abundant, the internal structures not usually being discernible (Plate 4.30). In samples showing background matrix fluorescence (e.g. SM18; Plate 4.30), much of this fluorescence

Plate 4.30 Low-magnification photomicrograph of liptinite-rich sediment showing *Botryococcus* fragments and fluorescing groundmass: blue-light excitation, oil immersion.

Cuniger Rock section, east Fife coast; sample SM 18.

x300

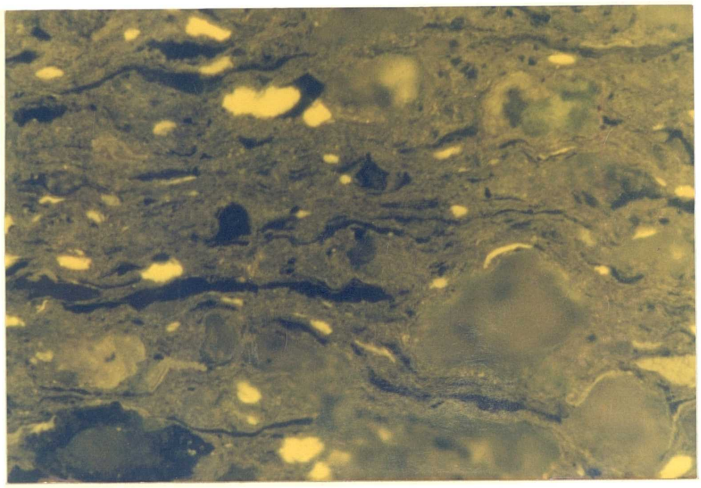


Plate 4.31 Higher-magnification photomicrograph of the above sample showing densely-packed discrete lamalginite in matrix and *Botryococcus* fragments: blue-light excitation, oil immersion.

x750

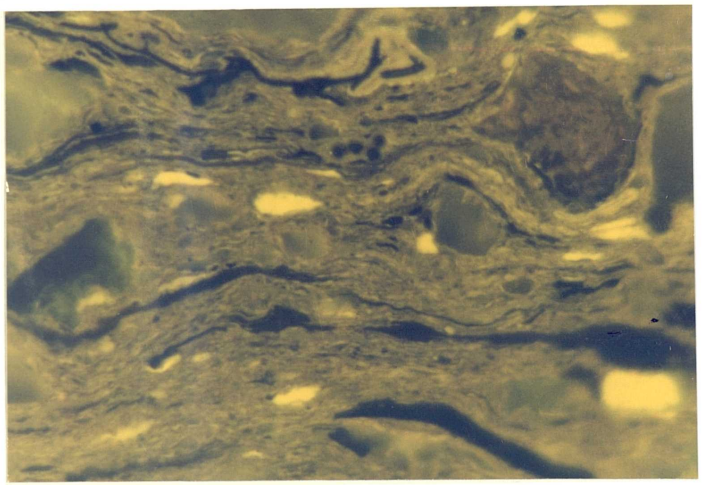
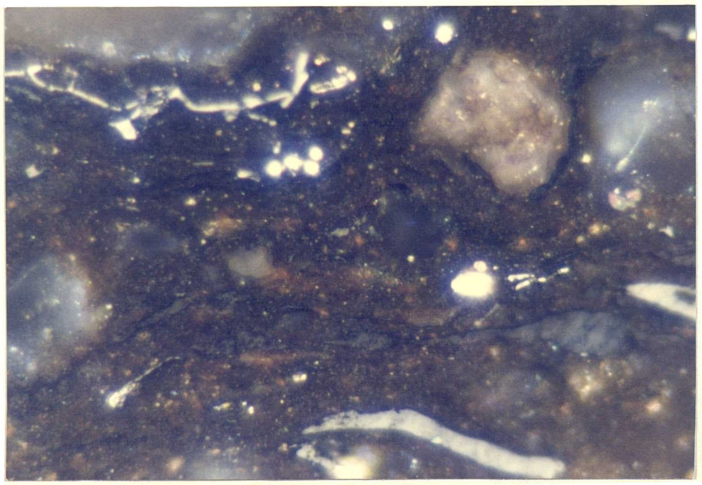


Plate 4.32 Same field of view as above: reflected light, oil immersion, plane-polarised light.

x750



is seen, upon higher magnification, to arise from densely-packed discrete lamalginite (Plate 4.31). Some of the groundmass fluorescence may also be due to the impregnation of the mineral matrix by free hydrocarbon material. The abundance of organic matter in the matrix and its intimate association with the mineral groundmass have imparted a dark overall stain to the mineral matrix (Plate 4.32). The presence of a dark mineral groundmass in reflected light is often indicative of a high liptinite content, which comprises lamalginite and/or liptodetrinite. The term "liptodetrinite" embraces constituents of the liptinite group which, because of their finely detrital state, cannot be assigned to a specific liptinite maceral group. The particle size is usually <5μm. In Midland Valley sediments, liptodetrinite may occur as fine wisps or flecks, and these qualifications (wispy or flecky) are made to the descriptions of liptodetrinite when such distinctions are apparent.

Plate 4.33 shows a mixed algal lithology where the matrix is filled with discrete lamalginite wisps. The sample is also rich in *Botryococcus* remains and is unusual because some bodies display an orange fluorescence and others fluoresce yellow, a phenomenon referred to again later. The internal morphological features of the telalginite are ill defined.

A unique algal-rich sample (sample Q) was discovered in the Anstruther Beds within the Billow Ness coastal section, near Anstruther (Plates 4.34-4.36). The sample contains at least three types of alginite within a highly calcareous mineral matrix. Moderate to intensely-fluorescing discrete lamalginite is the dominant constituent and occupies much of the groundmass as seen in sections perpendicular (Plate 4.34) and parallel (Plate 4.35) to bedding. Intensely-flurorescing, yellow, subspherical and elliptical telalginite is also a prominent constituent and, although no internal structures can be determined, the external morphology and size of these entities suggest that they are *Botryococcus* remains. The rarity of the sample stems from the presence of the third constituent which occurs in the form of discrete clasts and stringers containing layered lamalginite of the type reported in the Dunnet Shale, which enveloped calcite grains. Apart from *Botryococcus*, the botanical affinities of the two other algal types cannot be determined since, again, the intimate association between the liptinitic macerals and the mineral groundmass has prevented adequate separation of organic matter and its subsequent identification. What seems possible is that the algae in sample Q had different modes of life. The discrete lamalginite suggests a planktonic habit, whilst the layered lamalginite in the calcareous clasts was probably benthonic. A detailed assessment of the depositional environment of sample Q and the other shales discussed so far, based on morphological differences in the algae they contain, is given in Section 4.4.

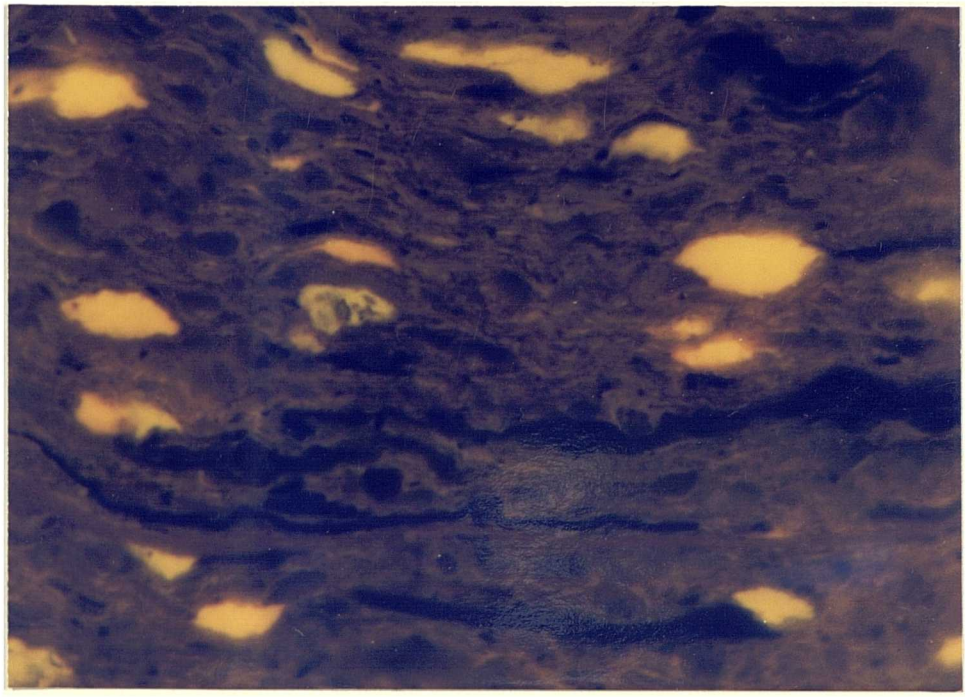


Plate 4.33 Mixed algal assemblage showing discrete lamalginite (matrix) and *Botryococcus* remains displaying orange and yellow fluorescence: blue-light excitation, oil immersion.

Billow Ness section, east Fife coast; sample Psh.

x750

Plate 4.34 Section perpendicular to bedding of a rare, algal-rich shale containing mixed algal assemblage consisting of discrete lamalginite, *Botryococcus* remains and clasts comprising layered (band) lamalginite enveloping calcite grains: blue-light excitation, oil immersion.

Billow Ness section, east Fife coast; sample Q.

x750

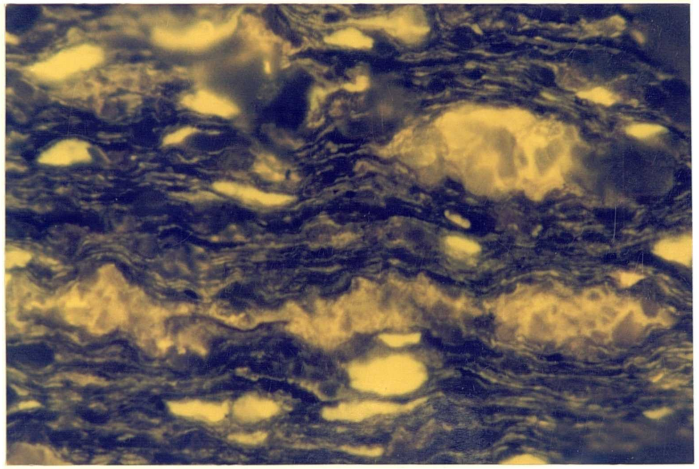
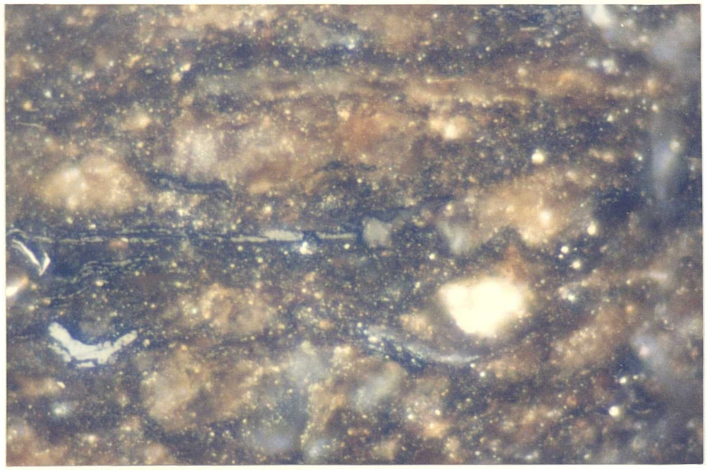


Plate 4.35 Section parallel to bedding of the above sample mainly showing discrete lamalginite (flecky appearance): blue-light excitation, oil immersion.

x750

Plate 4.36 Same field of view as Plate 4.35: reflected light, oil immersion, plane-polarised light.

x750



4.2.2 Coals and Related Materials

4.2.2.1 Humic Coals

Although no detailed studies have been made of coals in other UK Carboniferous provinces during this project, there are certain petrographic features which are highly characteristic of Midland Valley coals, but not necessarily exclusive to them.

The majority of coals in the Midland Valley fall within the category of humic coals since they are derived mainly from vascular-plant material which accumulated within peat-swamp environments. In keeping with other UK Carboniferous coals, the Midland Valley coals contain at least 60-70% vitrinite, most of which is in the form of band vitrinite ("vitrinite A" of Brown *et al.* 1964). Liptinite accounts for $\leq$10% of the organic matter, while various inertinitic components comprise approximately 20-30%. Much of the liptinite is represented by sporinite, usually in the form of thin-walled microspores. Cutinite is only a minor constituent although, when present, it tends to be exceptionally well preserved. Resin pods and droplets occur rarely, an observation consistent with the known lack of a widespread resin-bearing flora during Carboniferous times.

A notable feature of many low-rank coals (c.%$R_v \leq 0.70$) in the Midland Valley is the occurrence of vitrinite with exceptionally inhomogeneous surfaces, this material being colloquially referred to as "scruffy" vitrinite (Plate 4.37). The surfaces of such vitrinite have a patchy, mottled appearance through which the inherent telinitic cell structures can be discerned. Scratches from the grinding powder accentuate the heterogeneity of the vitrinite. Teichmüller (1974a) considered this texture to be due to the covering of the polished vitrinite surface by a smear film which she thought originated from liquid hydrocarbon exudates from within the sub-microscopic pore system of the vitrinite. Attempts to remove the film with water, IPA, DCM and petroleum ether failed; the only instance where the latent cell structure was revealed occurred fortuitously during the normal polishing procedure (Plate 4.38). Teichmüller (1974a) noted the disappearance of smear films following blue-light irradiation, which did not happen in the present study. Evidence supporting the release of lipoid material from vitrinite is contained in Plate 4.39 which shows the apparent expulsion of probable hydrocarbon material from cracks within the vitrinite matrix, giving rise to the formation of diffuse, Newton ring-type interference patterns. In the Midland Valley this phenomenon has so far only been recorded from Westfield Basin vitrinites, which are also exceptional because the development of "scruffy"

Plate 4.37 Typical inhomogeneous vitrinite surface formed by presence of a smear film: reflected light, oil immersion, plane-polarised light.

G coal, Westfield Basin; sample 3.

x750

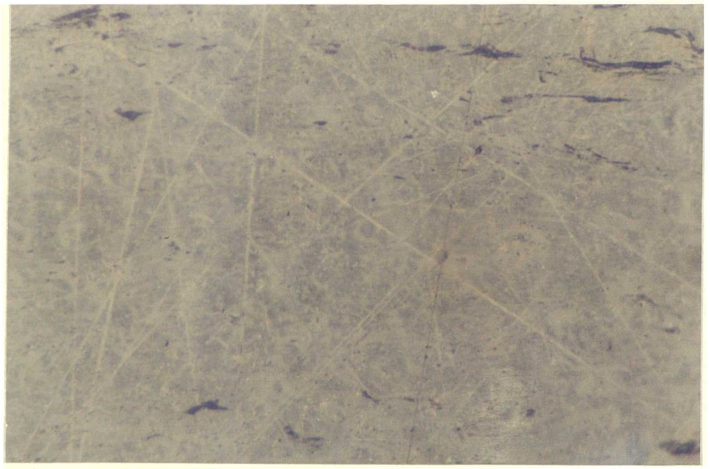


Plate 4.38 Removal of smear film (left) in inhomogeneous vitrinite to reveal latent cell structure (right): reflected light, oil immersion, plane-polarised light.

Vitrinitic clasts from Coalyard Neck, east Fife; sample A 43.

x750

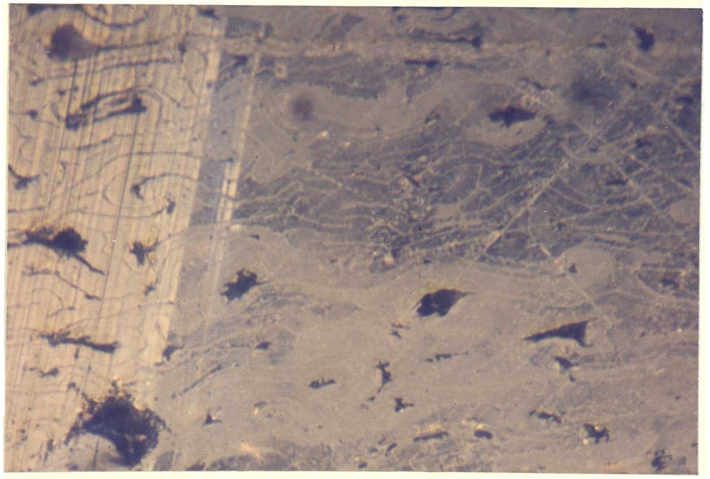
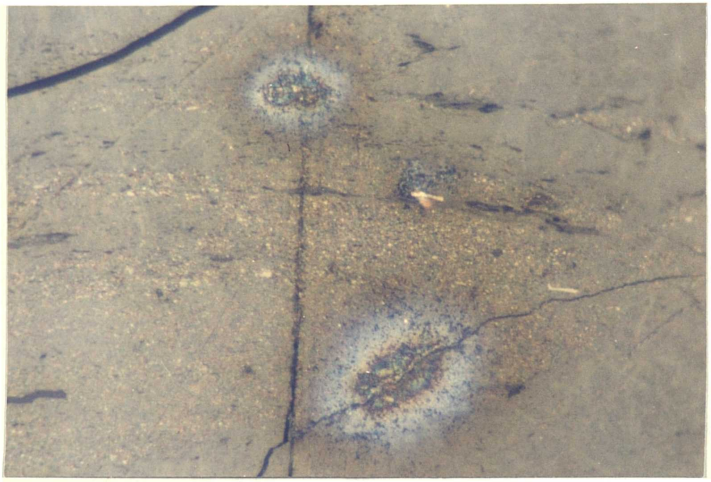


Plate 4.39 Typical hydrocarbon expulsion from cracks in vitrinite giving rise to Newton-ring effect: reflected light, oil immersion, plane-polarised light.

K coal, Westfield Basin; sample W15.6.

x750



vitrinite is nowhere more pronounced. Hydrocarbon expulsions from vitrinites of the form described above have been observed in coals from many localities worldwide where the vitrinites have been classed as perhydrous (Teichmüller 1974a; Stach *et al.* 1982). Many of these vitrinites display a strong fluorescence which is thought to be emitted from bituminous materials incorporated within the vitrinite structure. No fluorescing vitrinites were observed in samples from the Midland Valley.

In addition to the smear-film effect, the heterogeneity of many low-rank vitrinites often relates to the preservation of resinous cell contents in vitrinites (Plate 4.40). These resinous areas are often partly altered (Plate 4.41) or completely altered to micrinite. That much of this micrinitic matter is true micrinite and not granular humic material, mineral matter or micron-sized inertinite particles, which can all have a similar appearance to micrinite in reflected light, is inferred from the observations of similar micrinitic material that occurs in close association with liptinitic materials. High concentrations of micrinite also occur near to oil expulsions (Plate 4.39). Granular humic matter, inertinite and mineral matter do not show any particular association with hydrogen-prone organic matter (Taylor and Liu 1989). The iridescence seen in conjunction with some micrinitic areas may be due to the presence of *some* clay and/or granular humic matter. Besides their presence as discrete pods or stringers (depending on the orientation of the section), micrinite in Midland Valley coals is often finely dispersed throughout the vitrinite matrix (Plate 4.42). Transitions of resinous matter into micrinite have been observed in reflected light in many bituminous coals from different geological provinces (Teichmüller 1944; Benes and Pech 1967; Teichmüller 1974b), affording strong evidence that micrinite forms from liptinitic precursors. From these observations, which have been corroborated in recent studies using transmission electron microscopy (Taylor and Liu 1989), it is now accepted that micrinite is of secondary origin and forms from the disproportionation of liptinitic macerals to give liquid hydrocarbons on the one hand and a granular residue *viz.* micrinite on the other. The liquid-hydrocarbon product may either migrate from the sample or, in the case of a vitrinite-rich sample, may be retained within the vitrinite matrix because of the high absorptive capacity of the vitrinite (Teichmüller 1974a). The presence of dispersed micrinite in Midland Valley samples might therefore be attributed to the breakdown of hydrogen-prone material lying in interstices within the vitrinite structure.

In addition to the micrinite found within cell cavities and dispersed in the vitrinite groundmass, micrinite often occurs in close association with sporinite,

Plate 4.40 Resinous cell contents in vitrinite: reflected light, oil immersion, plane-polarised light.

G coal, Westfield Basin; sample 3.

x750

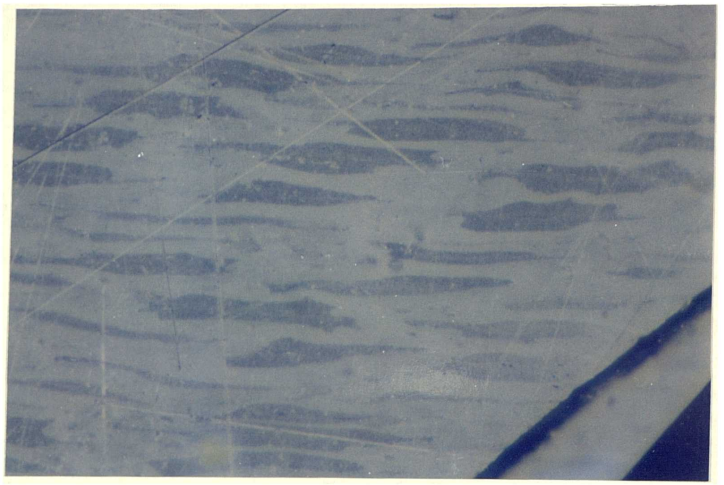


Plate 4.41 Incipient micrinite formation from resinous cell contents: reflected light, oil immersion, plane-polarised light.

Unnamed coal from Westfield Basin; sample 4.

x750

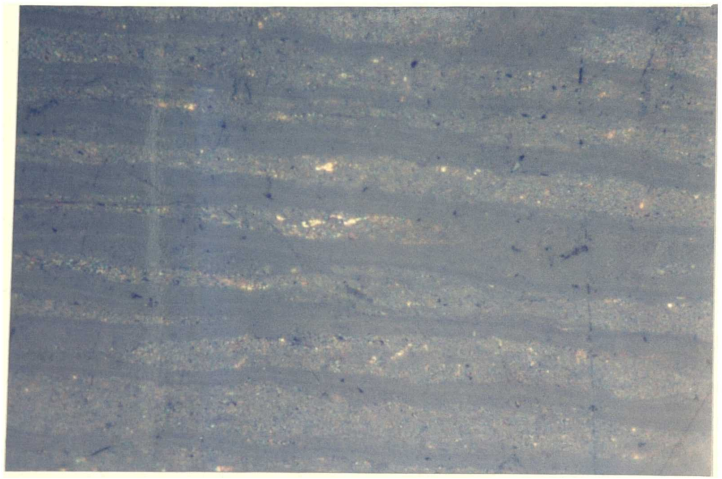
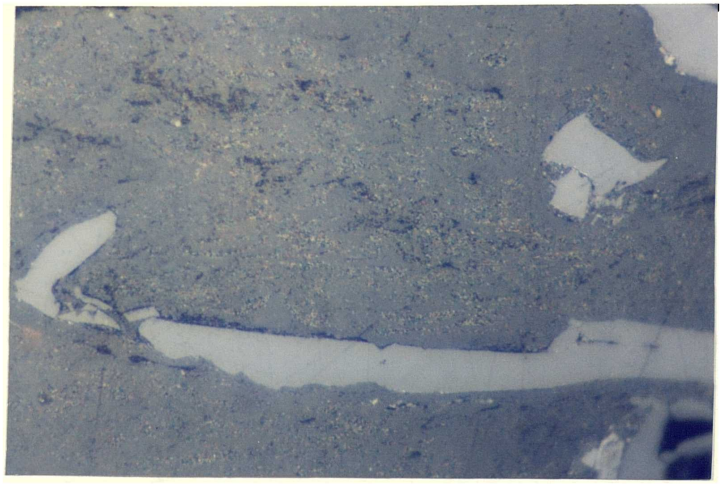


Plate 4.42 Dispersed micrinite in vitrinite from Westfield Basin: reflected light, oil immersion, plane-polarised light.

Unnamed coal from Westfield Basin, sample 4.

x750



particularly when the spores are concentrated in bands within the vitrinite. This association has long been recognised (Stach 1964) and, along with the observation that high concentrations of micrinite are found around the periphery of partially-decomposed spores (Diessel 1961), constitutes further evidence that micrinite originates from liptinitic precursors. Although micrinite in association with spores with degraded edges was not apparent in Midland Valley coals or sediments, the relationship between micrinite and sporinite was certainly sufficiently close in some coals for at least some micrinite to have derived from spores.

In summary, the "scuffy" appearance of many low-rank vitrinites in Carboniferous coals from the Midland Valley probably indicates that these vitrinites contain larger amounts of hydrogen-prone material than "normal" vitrinites of homogeneous appearance (i.e. the "scruffy" Midland-Valley vitrinites are perhydrous). Seepage of the incorporated bituminous matter to the surface of the section produces a smear film which imparts a marked heterogeneity to the vitrinite surfaces. Larger "accumulations" of bituminous matter may be released through cracks in the vitrinite. As coalification proceeds, the thermally-induced disproportionation of liptinitic progenitors produces dispersed micrinite, if the precursor material was the bituminous material in the vitrinite matrix, or the pod-like masses of micrinite if the progenitor liptinite was resinous matter infilling cell structures.

4.2.2.2 Sapropelic Coals (excluding torbanite)

The sapropelic coals constitute the second major division of coals found within the Carboniferous of the Midland Valley. Individual coals comprise an ill-assorted mass of finely comminuted humic and liptinitic debris, the latter usually exceeding 10%, and sometimes very finely laminated. The sapropelic coals are of restricted aereal extent in keeping with their formation as accumulations of organic-rich ooze within pools in peat-swamp environments. The coals are represented mainly by cannels in which the liptinitic components are dominantly sporinite. Accumulations of large quantities of *Botryococcus braunii*, which flourished in aerated, ulmin-free surface waters of peat-swamp pools (Moore 1968), give rise to the torbanite and torbanitic shales described in Section 4.2.1.2. The cannel coals can be traced laterally into humic coals (Conacher 1917; MacGregor 1938), but they may also occur as bands and lenses within such coals (e.g. Plate 4.43). This mode of occurrence suggests that periodic expansions of the pool occurred, causing deposition of sapropelic material within the environment dominated by humic-coal deposition.

Plate 4.43 Cannel band in humic coal: reflected light, oil immersion, plane-polarised light.

Stairhead seam, Monkton House Borehole, Lothians; sample 1686.

x750

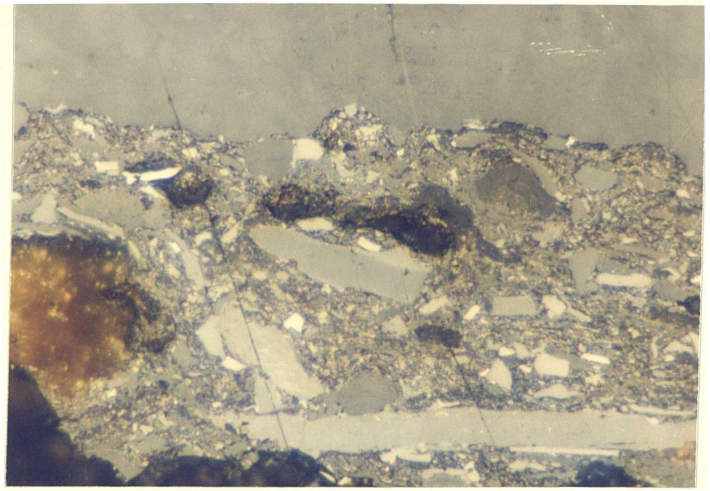


Plate 4.44 Cannel coal, Methil, Fife: reflected light, oil immersion, plane-polarised light.

Precise locality unknown; Hunterian Museum sample M4197.

x750

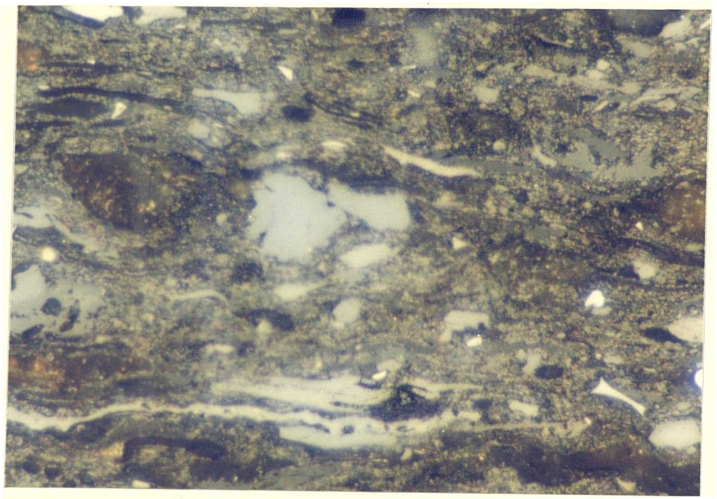
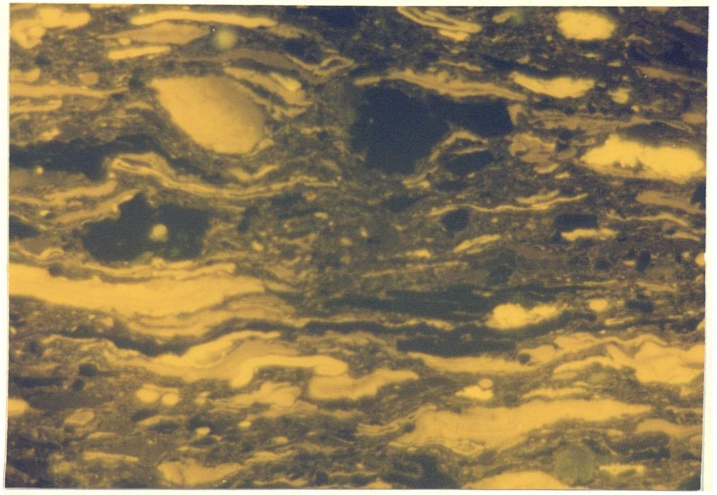


Plate 4.45 Approximately same field of view as above: blue-light excitation, oil immersion.

x750



The characteristic feature of Midland Valley cannel coals, as with other similar deposits, is the abundance of micrinite which constitutes much of the granular matrix in which the other debris are set (Plates 4.43 and 4.44). The hydrogen and volatile-matter yields of cannel coals have long been recognised as being higher than those of humic coals at an equivalent level of coalification (Krȍger 1968; Kunstner 1974) due to the enrichment in hydrogen-prone organic matter that occurs in the environments in which these deposits accumulated. That these deposits contain much hydrogen-prone material is clear from the matrix fluorescence displayed after blue-light irradiation for several minutes (Plate 4.45). Thus, although some micrinite may be derived from discrete liptinitic components, for example sporinite (see Section 4.2.2.1), the greater part of the micrinite probably originates from the disproportionation of the hydrogenous matter that saturates the cannel matrix.

Most of the liptinite in Midland Valley cannels comprises thin-walled spores, although liptodetrinite is also abundant (Plate 4.45). The fluorescence colour and intensity of the liptodetrinite suggests an origin in spore material rather than algae. The algae found within cannels is nearly always *Botryococcus* telalginite. Lamalginite in Midland Valley cannel coals is exceptionally rare. Only one example of a lamalginite-containing cannel was found during this project (the Houston Coal, from Burntisland; Plates 4.46 and 4.47). The finely-laminated nature of this sample and its high liptinite content are clearly indicative of deposition in a sapropelic environment. In addition to the sporinite and *Botryococcus* telalginite present, the coal contains abundant discrete lamalginite wisps (Plate 4.47). The deposit therefore falls under the heading of a lacositic coal, as defined by Cook (1988), i.e. a sapropelic coal in which the liptinite component is dominated by lamalginite. Such deposits are rare.

The "contamination" of cannel coals by clay minerals results in the formation of canneloid shales in which the detrital nature of the deposit is still readily apparent (Plates 4.48 and 4.49). Many canneloid shales contain vitrinite in the form of ramifying wisps and stringers in contrast to discrete bands or particles. This "stringy" type of vitrinitic material was also found within the torbanite and torbanitic shales (see Section 4.2.1.2).

4.2.2.3 Woody and Vitrinitic Materials

Humic materials in the form of wood fragments and carbonised plant remains have long been known to occur within volcanic successions in Fife (Geikie 1879, 1902; Kidston 1907) and the Lothians (Cadell 1892; Geikie 1900; Gordon 1938). Most of the plant material found within volcanic sequences is preserved in

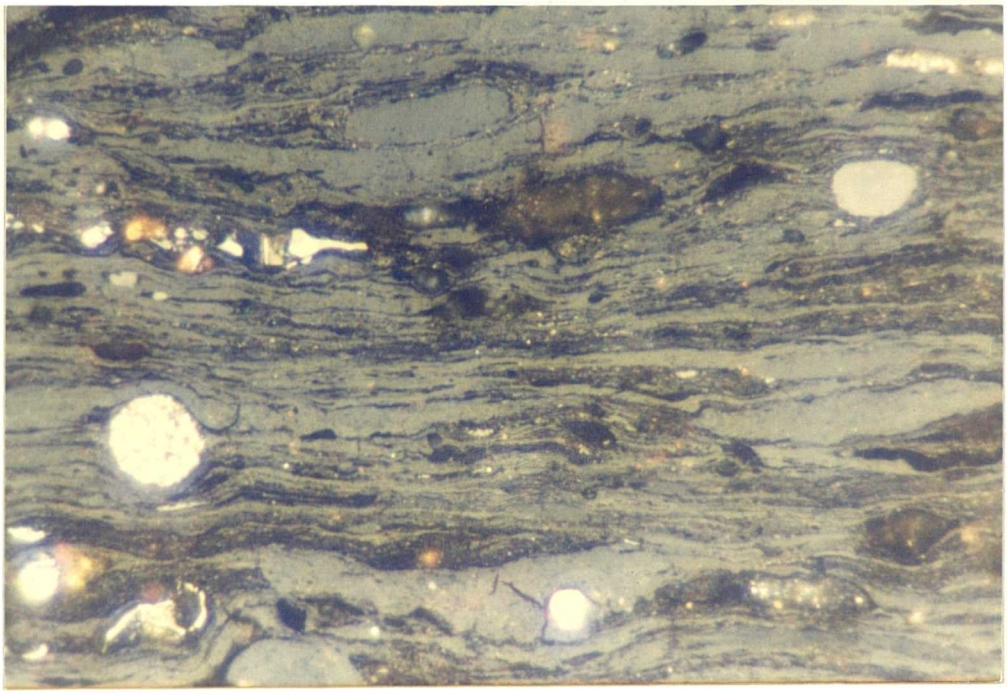


Plate 4.46 Lacositic coal: reflected light, oil immersion, plane-polarised light.
Houston Coal, Binnend Tip, Burntisland; sample BINN.
x750

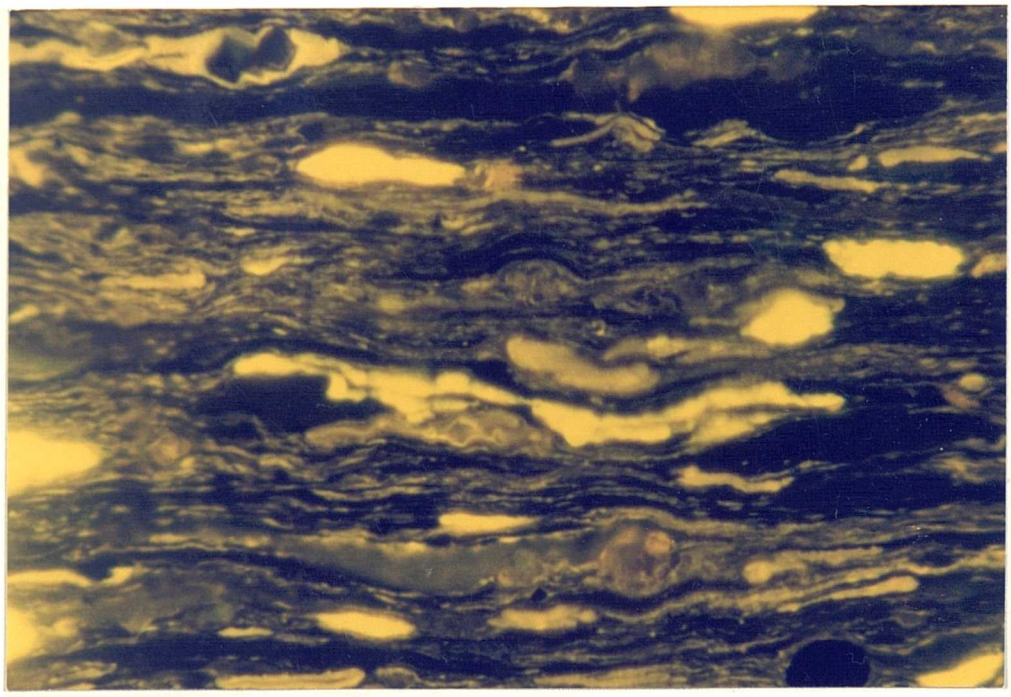


Plate 4.47 Same sample as above: blue-light excitation, air.
x750

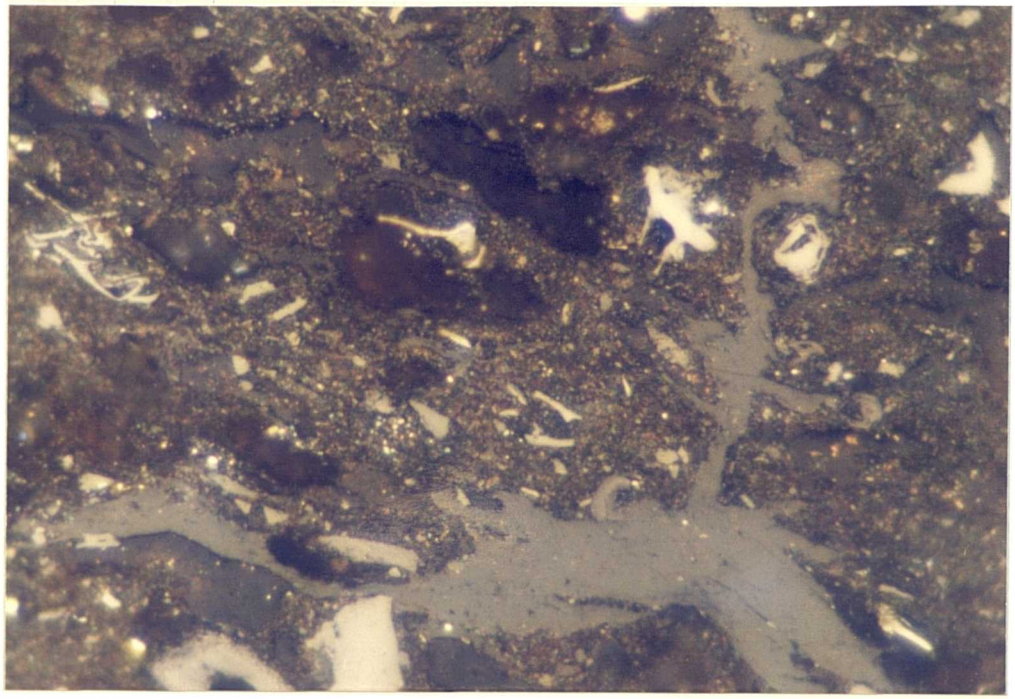


Plate 4.48 Canneloid shale with ramifying, wispy vitrinite stringers. Deep brown blobs are *Botryococcus* telalginite, dark grey components are sporinite and spore debris: reflected light, oil immersion, plane-polarised light.

Section west of St.Monance; sample 5A1.

x750

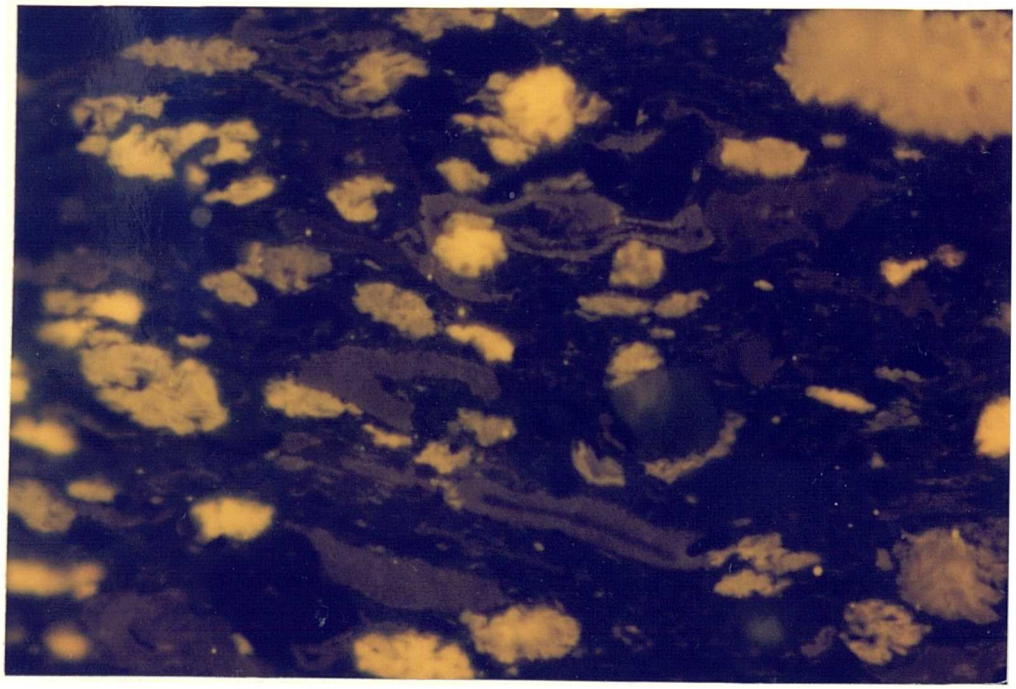


Plate 4.49 Same sample as above: blue-light excitation, oil immersion.

x750

sediments that are intercalated with volcanic rocks or within sediment boulders which have been subsequently incorporated within lavas or pyroclastic materials (see Scott and Rex 1987 for a review). The preservation of flora within volcanic ashes *per se* is relatively rare: woody fragments have been reported from vents outcropping along the east Fife coast (Geikie 1879, 1902), and petrified plant remains have been collected from localities within the tuffs of the Arthur's Seat Volcanics (Campbell 1917) and Garleton Hill Volcanics (Scott *et al.* 1984; Scott and Rex 1987). A detailed study of some woody material found in a vent was considered appropriate, following the discovery of an exceptionally well-preserved specimen from Orrock Quarry, central Fife. The analysis of this wood presented a rare opportunity to investigate a precursor of much of the terrestrially-derived organic matter occurring within the Carboniferous succession in the Midland Valley.

The wood sample was found on the upper bench of Orrock Quarry in an ash-filled volcanic pipe which cuts a lower Carboniferous basaltic lava. The exact stratigraphic position of the sample is unknown, but the vent system at the quarry lies within part of the Burntisland Volcanic sequence which lies within the Calciferous Sandstone Measures (i.e. Viséan). The sample occurred in a green, lithic tuff which itself contains abundant smaller wood fragments (Plate 4.50). In hand specimen, veins and small vugs of calcite can be seen within both the wood sample and the enclosing pyroclastic material. In transmitted light (Plate 4.51), the tuffaceous matrix is seen to be highly degraded, comprising a mélange of lava fragments and crystalline material set in a heavily carbonate-impregnated matrix. The most striking feature about the wood is its relatively unaltered state and the remarkable degree of preservation of the cell structures and their contents. The conducting elements (probably tracheids) are still clearly visible in transmitted light under low magnification (Plate 4.51). In reflected light, depending on the cut of the section, a range of cell structures was encountered. The transverse section in Plate 4.52 shows the uncompressed character of the cells which are filled with material that appears to be dominantly micrinitic, but which may also contain clay and fine granular humic matter that probably contributes to a granular, micrinitic appearance (Taylor and Liu 1989). In some of the cell contents, vacuoles and pores have developed, perhaps indicating the release of volatiles. In other cells, the contents, as well as being vacuolated, have shrunk and have become detached from the cell walls. These observations are suggestive of mild heating, although the sample is immature since the oil reflectance of the cell walls is only 0.39 per cent.

Plate 4.50 Hand specimen of wood lying in lithic tuff.

Plate 4.51 Wood fragment in lithic tuff showing conducting elements: transmitted light, air.

Plate 4.52 Uncompressed cells in wood, mostly filled with probable micrinite-clay-granular humic mixture and some of the contents showing development of vacuoles: reflected light, oil immersion, plane-polarised light.

Plate 4.53 Uncompressed cells with mineral-filled cavities, showing staining by bituminous/humic exudate: reflected light, oil immersion, plane-polarised light.

Plate 4.54 Longitudinal section of wood illustrating two types of degradation zone: SR, soft-rot fungi; VM, various micro-organisms: reflected light, oil immersion, plane-polarised light.

Plate 4.55 Soft-rot fungi penetrating wood in uncompressed zone: H, hyphae; SH, other hyphal forms; M, middle lamella: TEM.

Plate 4.56 Various micro-organisms in relatively disturbed zone of cells: C, microbial cells; M, middle lamella; F, long fibres; SW, secondary walls; P, phosphate mineral: TEM.

Plate 4.57 Various micro-organisms in relatively disturbed zone of cells: C, microbial cells; H, filamentous hyphae; G, granular humic acids; M, middle lamella; SF, stain fungi; P, phosphate minerals: TEM.

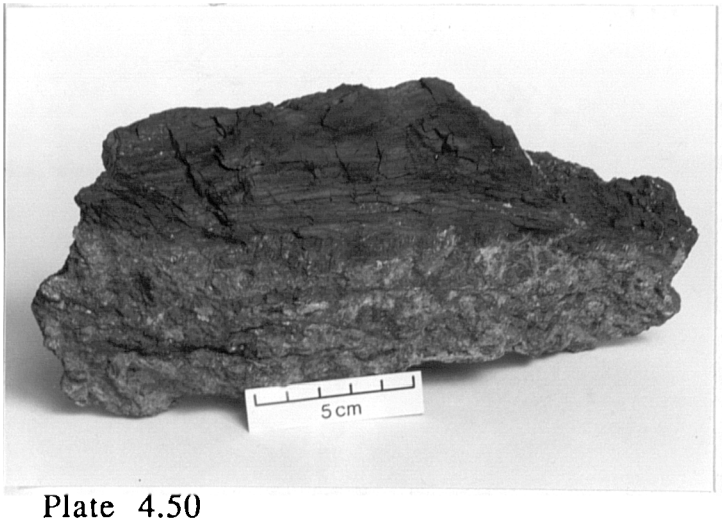


Plate 4.50

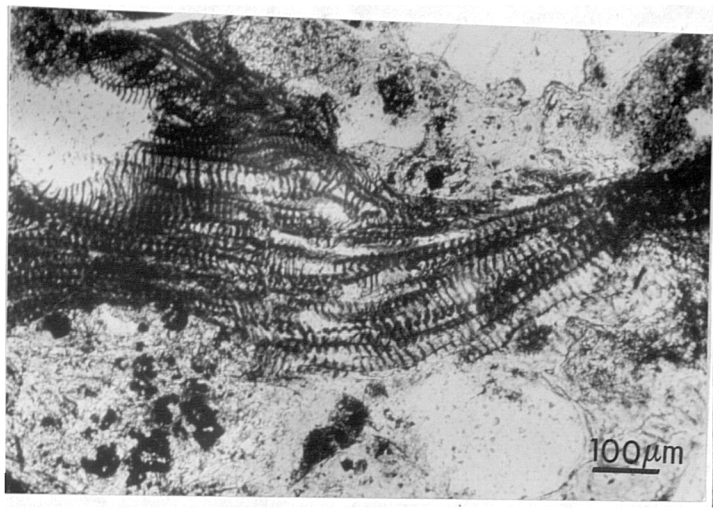


Plate 4.51

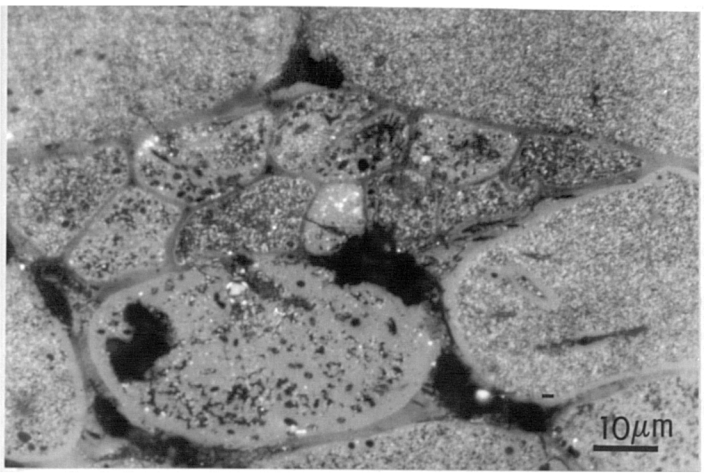


Plate 4.52

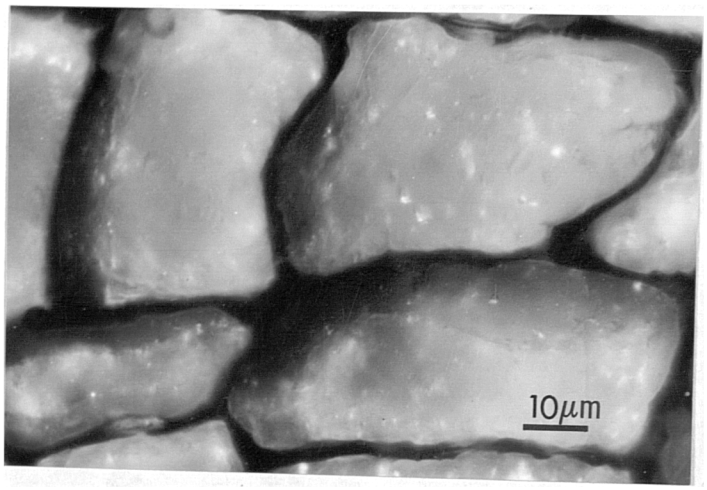


Plate 4.53

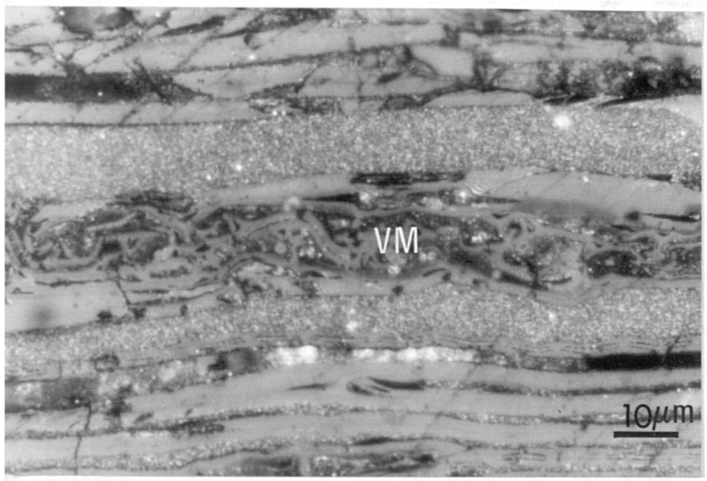


Plate 4.54

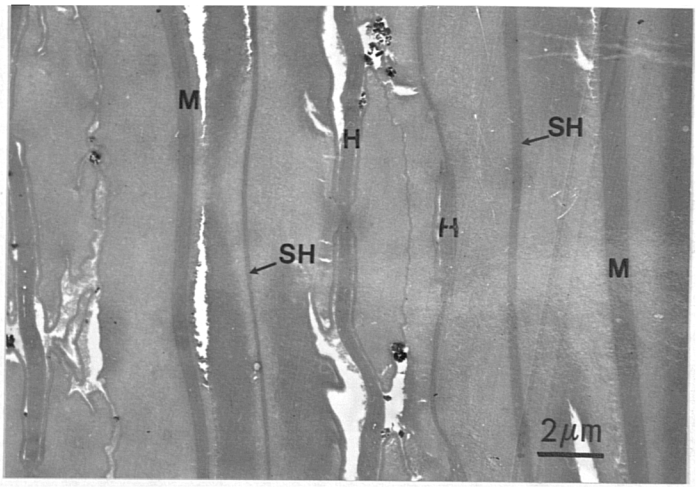


Plate 4.55

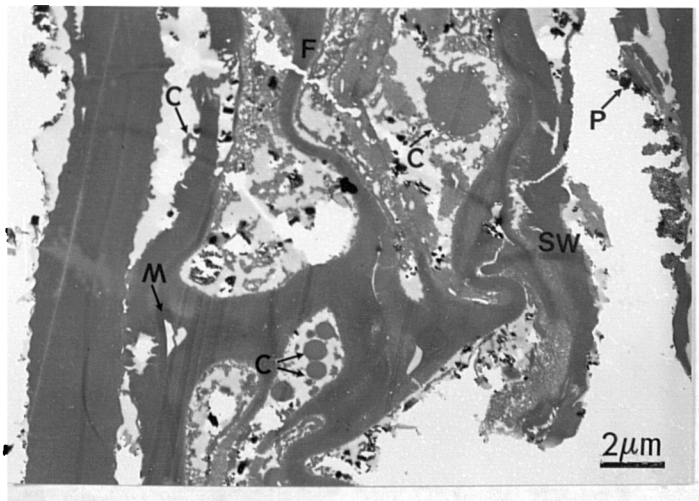


Plate 4.56

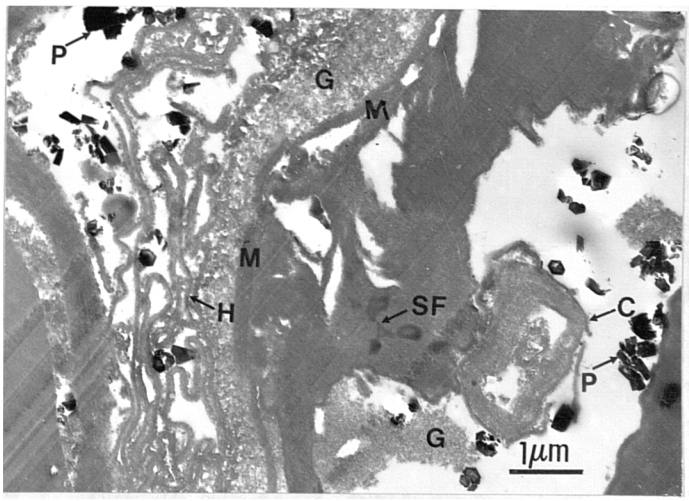


Plate 4.57

Many of the uncompressed cell lumens in the wood are filled with mineral matter, principally calcite, with only the thin, lignified cell walls remaining (Plate 4.53). The diffuse, dark areas shadowing many of the cell walls represent a brown staining of the mineral material by what is probably a humic and/or bituminous substance that has exuded from the cell walls. Longitudinal sections of the wood (Plate 4.54) reveal two types of structural zone, one in which long fibres of tissue are uncompressed and remain largely unbroken, sometimes separated by vessels containing the micrinitic/clay/humic acid granular mixture, and a second, in which the cell remains are much more disorganised and disturbed than elsewhere. These remains are difficult to resolve by light microscopy, but recourse to transmission electron microscopy (TEM) allowed a much more precise definition of the wood structure. The TEM technique has already been successfully used to elucidate the fine structure of some Australian coals (Taylor *et al.* 1982; Taylor and Liu 1987). TEM of material from the Midland Valley was undertaken by S.Liu and G.H.Taylor at the Australian National University, and subsequent discussions of the TEM data are based on personal communications from these workers. Ultra-thin sections were cut with diamond knives, and some sections were stained with uranyl acetate and lead citrate to enhance selectively the electron density of some components.

From the TEM analysis of the Orrock wood it is apparent that the two structural zones shown in Plate 4.54 represent areas in which two main types of biodegradation have occurred. The first, relatively undisturbed, zone is characterised by the presence of soft-rot fungi. These organisms usually attack wood under moist conditions , and they are generally most abundant within the surface layers of peats. In the wood, the soft-rot fungi appear as conical-ended hyphal segments which run approximately parallel to the direction of the middle lamellae (Plate 4.55). The soft-rot fungi attack the wood by depolymerising the cellulose and other polysaccharides. The fungi cannot usually utilise lignin, which is left behind in the form of granular humic acids. Due to a high lignin content, the middle lamellae and their adjacent lignified cellulosic layers resist the attack of soft-rot fungi and may retain their form until the final stages of decay.

The biodegradation that occurred in the more disturbed zones (Plate 4.54) is thought to be much more complex than simply a stage in the degradation by soft-rot fungi. Plates 4.56 and 4.57 are TEM photomicrographs showing the typical appearance of the disorganised zones. In Plate 4.56, a band of severe degradation appears to have terminated against a middle lamella. More than one type of fungus was probably active in the degradation process,

as revealed by the presence of "stain fungi" (SF) acting on a cellulose wall (Plate 4.57). The granular layer adjacent to the bundles of long, thin hyphae probably represents another residuum of fungal degradation. Varying degrees of granularity are discernible in the hyphae, suggesting that the fungal remains themselves have been attacked by other micro-organisms, possibly bacteria. Although the small, solid, circular bodies, particularly noticeable in Plate 4.56, resemble coprolites of microfauna, the bodies in the Orrock wood are much smaller and, consequently, are probably microbial cells (G.H.Taylor *personal communication*). One of these spherical bodies in the top right hand side of Plate 4.56 appears to have been attacked by other microbes, probably of bacterial origin.

The repetition of bands in which degradation was severe occurs throughout the sample and may be related to a predisposing feature of the wood, for example, the presence of vessels through which nutrients could pass readily, thus enhancing microbial activity. The TEM photomicrographs also show dark, electron-dense areas occupied by mineral matter. Electron-diffraction studies have established that these crystals are phosphatic and have the composition $Ca_2P_2O_7.2H_2O$. All crystals occur in cell cavities and not within cell walls.

Studies of Carboniferous plant material from other volcanic provinces in the Midland Valley have also revealed the presence of exceptionally well-preserved uncompressed cell structures, particularly when preservation has been accomplished through permineralisation (Scott *et al.* 1984; Rex and Scott 1987; Scott and Rex 1987; Scott and Galtier 1988). Permineralisation involves the infiltration of cell lumens by mineral solutions before the cell walls were compressed and before the onset of severe microbial decay, thus accounting for the exquisite preservation of internal cell structures and their contents. In the Midland Valley, permineralised samples within volcanic sequences are mainly calcareous (Scott and Rex 1987). The carbonate is thought to originate from the breakdown of calcium-bearing components present in volcanic ashes. Such substances include olivine, calcic plagioclase and palagonite (derived from volcanic glass), all of which are abundant in the basaltic pyroclastics found in the vents of Fife and the Lothians. In the samples investigated by Scott and co-workers and in the Orrock wood, the calcite does not replace plant matter, but simply infills cell lumens. This feature, coupled with the observation that the phosphate minerals in the Orrock wood occur only within cell cavities, suggests that there has been little, if any, interaction between mineralising solutions and cell walls in plant debris incorporated within volcanic ashes in the Midland Valley.

Plate 4.58 Hand specimen of nodule from East Kirkton Quarry.

The petrographic characteristics displayed in the Orrock wood sample are not unique. Despite being black and of vitrinitic appearance, fragments found within a small vent on the floor of Orrock Quarry were of a similar type (and rank) as the woody material collected from the upper bench. The vitrinite-like clasts displayed a high degree of cellular preservation, contained bands of much disorganised cellular contents of the type shown in Plate 4.54 and were also heavily calcitised. Calcitised, vitrinite-like material displaying petrographic features comparable with those of the Orrock samples was obtained from vent tuffs at various localities along the east Fife coast (see, for example, sample descriptions A43, KIN16, KIN20 and C from the Kincraig, Elie Harbour and Coalyard Hill necks). Although the petrographic characteristics equate with those observed in the low-rank organic matter from Orrock Quarry, the coaly-looking material from the east Fife vents has attained bituminous rank on the basis of oil-reflectance data. The recognition of zones in which cell contents are severely disrupted (Plate 4.54) has not been achieved in Midland Valley coals using reflected-light microscopy. Thus, it appears that the vitrinitic material from the Fife vents, referred to above, may more appropriately be referred to as high-rank wood rather than *bituminous-rank vitrinite sensu stricto* (i.e. one which has passed through a gelification stage thereby leading to the elimination of cellular structures with fine detail). Further discussion of this issue in relation to clasts found in Fife vent deposits is given in a later chapter.

Another example of what is thought to be permineralised organic matter is represented by the calcareous concretionary structure shown in Plate 4.58. This sample came from the laterally-impersistent East Kirkton Limestone, exposed in East Kirkton Quarry, near Bathgate. The limestone unit lies within a thick lava sequence in the Upper Oil-Shale Group. The limestone is unusual because it is highly spherulitic, contains bands with highly contorted laminae and beds of chert nodules. Such an assemblage is thought to have formed from calcareous muds that accumulated in a shallow volcanic pool associated with hot springs. The pool also received periodic influxes of organic matter (Muir and Walton 1957). The limestone has yielded an unusual flora and fauna (e.g. amphibians, spiders etc; see Wood 1985 for review) which are consistent with the proposed freshwater origin for this sample.

Microscopical examination revealed that the organic matter at the centre of the concretion was vitrinite which was very heterogeneous in places and contained patches showing incipient micrinitisation. TEM analysis revealed the presence of soft-rot fungi of the type found in the Orrock wood and also zones in which various microorganisms of the types seen in Plates 4.56 and 4.57 occurred.

An interesting difference between the Orrock and E.Kirkton material is that the different types of biodegradation zone were not detectable by reflected-light microscopy in the E.Kirkton vitrinite. A further significant difference is that the middle lamellae of the vascular plant-cell walls in the Kirkton material have not been preserved, whereas they are discernible in the Orrock samples.

The concretionary nature of the sample and its calcareous lithology comply with the descriptions of many coal-ball structures which have been found within Carboniferous strata in Europe and America (Scott and Rex 1985). Coal balls are limestone concretions representing peat fragment which have been mineralised, usually when the peat is *in situ*. The fine anatomical and histological details preserved in the organic matter found within coal balls is consistent with the mineralisation having occurred before appreciable compaction of the peat and before the onset of severe decay. Although no plant-bearing coal balls *sensu stricto* have been found within volcanic sequences in the Midland Valley, plant-bearing lithologies in which the mode of mineralisation closely resembles that of coal balls have been reported (e.g. at Pettycur; Rex and Scott 1987), mineralisation having occurred while the peat was still in place.

The detailed study of modes of plant preservation lies outside the scope of the present project, but the retention of the two types of biodegradation zone in the Kirkton vitrinite suggests that the timing of mineralisation is akin to that in coal-ball peats, i.e. it occurred during or shortly after peat deposition. That the two zones of biodegradation are not discernible in reflected light suggests that the subsequent increase in rank of the sample (to $\%R_o av=0.53$) has been accompanied by gelification of the organic matter which has obscured or eliminated the histological details of the vitrinite to a degree sufficient to make them undetectable in reflected light, but still detectable by TEM. Failure to detect any middle lamellae in the Kirkton sample using TEM also supports the opinion that the vitrinite has gone through a gelification stage during which the delicate tissues of the plant-cell walls have disappeared (G.H.Taylor *personal communication*). The process through which the vitrinite in the East Kirkton sample gained its present rank thus conforms to traditional coalification, i.e. progression into the bituminous- rank range following a gelification stage. This process contrasts markedly with that thought to be responsible for rank increase in the vitrinite samples from the east Fife vents. As mentioned earlier, the east Fife vent samples are of bituminous rank, but, unlike all other vitrinites of similar rank that have been examined, they still retain fine cellular details which are readily discernible in reflected light. The inference, therefore, is that these "vitrinites" have not passed through a gelification stage. Further implications of this inference are dealt with in Chapter 5.

Whether the mineral solutions percolated through the peat as it was developing or after fragments were incorporated within the calcareous sediments of the volcanic pool is not known. The occurrence of the concretionary, vitrinite-bearing sample within limestone, which itself is spherulitic, make the second alternative more likely. A possible scenario envisages a peat fragment being washed into the pool in which carbonate-bearing solutions mineralised the organic matter. The peat fragment also acted as a nucleus around which calcite accreted, thus giving rise to the nodular, coal ball-like morphology of the sample.

4.2.3 Marine Horizons

Almost all of the samples used to investigate organic-matter type variation within marine horizons were obtained from named marine bands (e.g. Queenslie Marine Band) or from marine shales associated with some of the geographically-widespread marine limestones which serve as important stratigraphic markers in the area. The samples were examined petrologically and geochemically to ascertain any variation in organic-matter type, not only within the same stratigraphic interval, but within different marine shales throughout the Carboniferous succession. The samples also form the basis of the majority of rank maps discussed in Chapter 5.

4.2.3.1 Queenslie Marine Band

This major Westphalian marine horizon separates the Lower and Middle Coal Measures (see p.32). Descriptions of the fauna occurring within the Queenslie Marine Band and its geographic distribution are presented in the work of Brand (1977). Most of the samples from the Fife and Stirling-Clackmannan-Central Coalfield Basins investigated in this thesis are documented within the latter publication; they are prefixed "QMB" in the Appendix.

The lithology in the Queenslie Marine Band samples studied is predominantly shale with subordinate siltstone. The mineralogy of samples varies in that they may be markedly calcareous or pyritic with various intermediates. The organic content of the samples is variable, and inertinite macerals generally dominate the maceral assemblages. Despite being of marine origin, the majority of Queenslie Marine Band samples contain at least 5-10% vitrinite. Increasing liptinite content is accompanied by a darkening of the matrix stain, and in some samples the mineral groundmass may take on the appearance of being completely impregnated with bitumen (referred to as matrix saturated in the sample descriptions: see also Plate 4.59). The most abundant liptinitic component is

Plate 4.59 Pyritic shale sample of Queenslie Marine Band with the rock matrix saturated with organic matter: reflected light, oil immersion, plane-polarised light.

Arden 5 Borehole, Central Coalfield; sample QMB 69.

x750

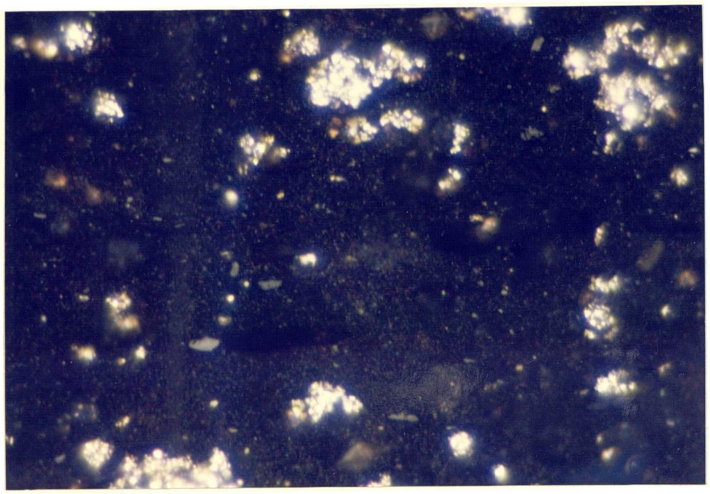


Plate 4.60 Same sample as above, section perpendicular to bedding, showing thin-walled miospores, liptodetrinite (disseminated through matrix) and thick-walled algal body (bottom): blue-light excitation, air.

x750

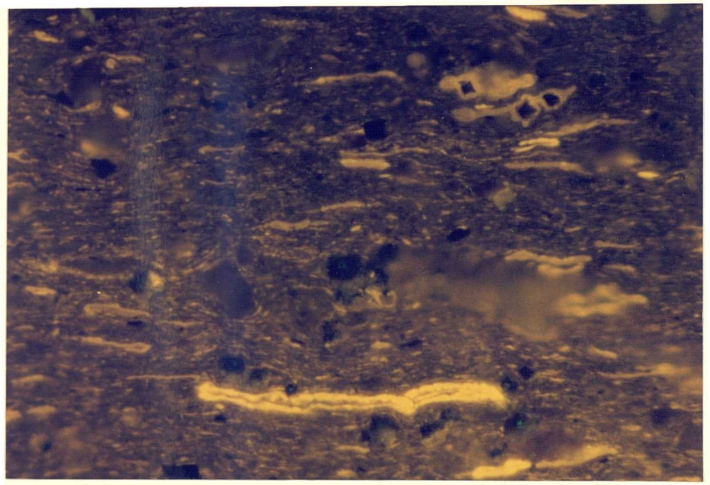
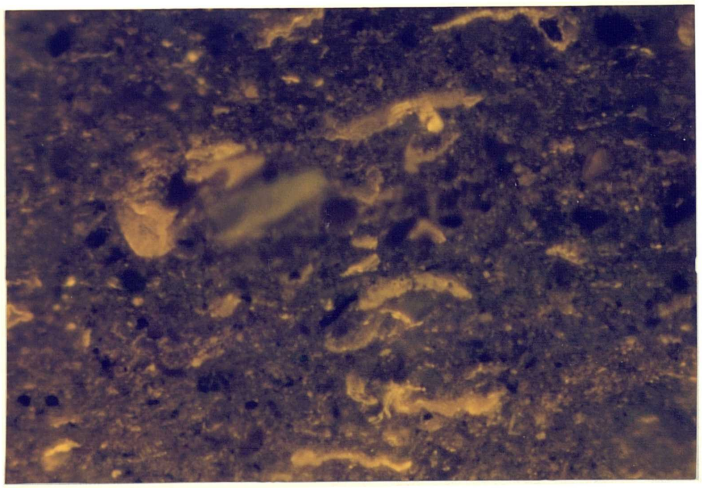


Plate 4.61 Same sample as above, section oblique to bedding, showing thin-walled miospores (diffuse) and liptodetrinite flecks: blue-light excitation, air.

x750



liptodetrinite which is much finer (1-3μm) than observed in other samples described so far (compare, for example, Plate 4.60 with Plates 4.45 and 4.49). Liptodetrinite is disseminated throughout the whole mineral matrix, and it probably constitutes the remains of marine phytoplankton. The fine, wispy entities of Plates 4.60 and 4.61 (*c.*20-40μm) which display moderate, orangey-yellow fluorescence were, on the basis of their thinness, considered initially to be of algal origin. A detailed examination of many marine and non-marine sediments containing these moieties suggested that they were probably exceptionally thin-walled miospores (also supported by A.C.Cook, *personal communication*). Although not apparent from the photomicrographs, the spores do not fluoresce as intensely as the liptodetrinite material.

Another common component within the liptinite fraction is represented by discrete lamalginite. In sections cut perpendicular to bedding (Plates 4.62 and 4.63), these appear as discrete wisps *c.10-20*μm in length, but in sections cut parallel to bedding (Plate 4.64) they appear in the form of isolated, cyst-like structures. The high fluorescence intensity of these lamellar entities suggests that they are probably of algal affinity. A third, probably algal, liptinite constituent found within the Queenslie Marine Band is illustrated by the intensely-fluorescing, double-walled structure in Plate 4.60. These structures are generally 50-70μm long, but may approach 200μm in some samples. Similar entities were found within some of the Lothians-type lamosites (see Plate 4.7).

Telalginite derived from the remains of *Tasmanites* has been reported as an important contributor to the organic matter of many marine sediments (Hutton *et al* 1980; Cook *et al* 1981; Sherwood 1984). Algal bodies bearing a resemblance to *Tasmanites* (e.g. Plate 4.65) were found in only three Queenslie Marine Band samples, all of which lie in the Central Coalfield (samples QMB18, QMB73, QMB74). Since only one tasmanitid was noted in each of these samples it is obvious that this algal type is rare within the Queenslie Marine Band horizon.

No variation in the proportion of liptinitic constituents was noted within the differing lithologies, but a decrease in the proportion of vitrinite contributing to the organic assemblages was noted as the sediments became increasingly calcareous. Marls (Plates 4.66 and 4.67) contained only trace amounts of vitrinite, the bulk of the organic matter being represented by liptodetrinite flecks.

A feature of particular interest is the nature and occurrence of the material shown in Plates 4.68 and 4.69. It exists in the form of diffuse "splodges" (Plate 4.68), discrete particles (Plate 4.69) and as fine wisps. This material has a fine granular mosaic texture. Laboratory carbonisation experiments and observations of textural changes in organic matter in the natural environment

Plate 4.62 Section cut perpendicular to bedding of a Queenslie Marine Band sample containing discrete lamalginite: reflected light, oil immersion, plane-polarised light.

Frances Colliery Bore, Fife-Midlothian Basin; sample QMB A43.

x750

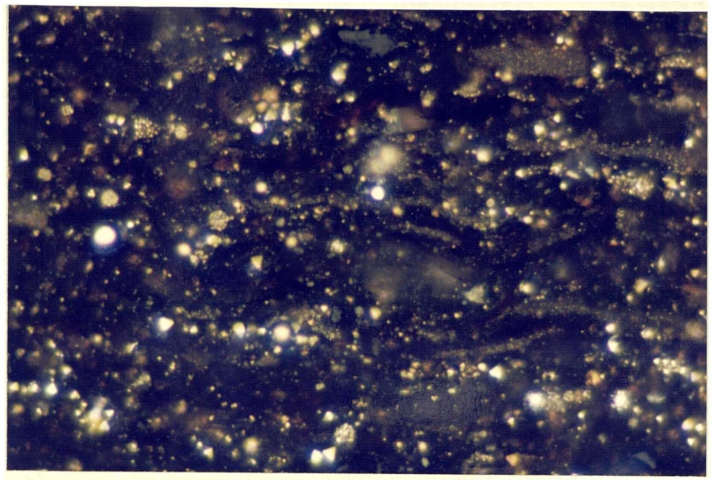


Plate 4.63 Same field of view as above showing discrete lamalginite wisps and spores (top right): blue-light excitation, oil immersion.

x750

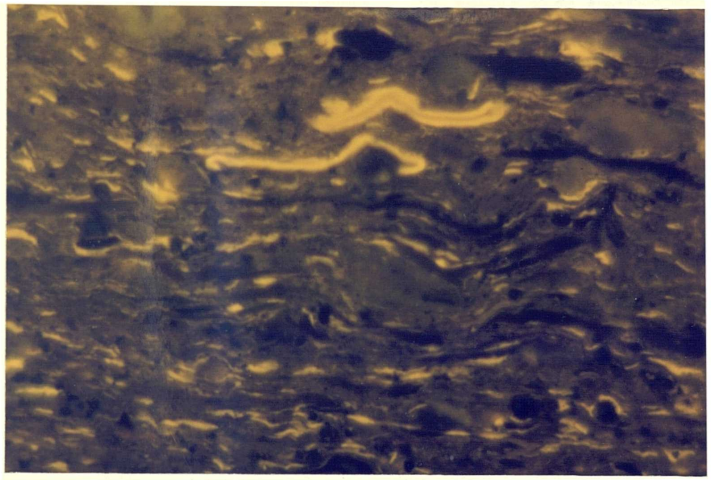
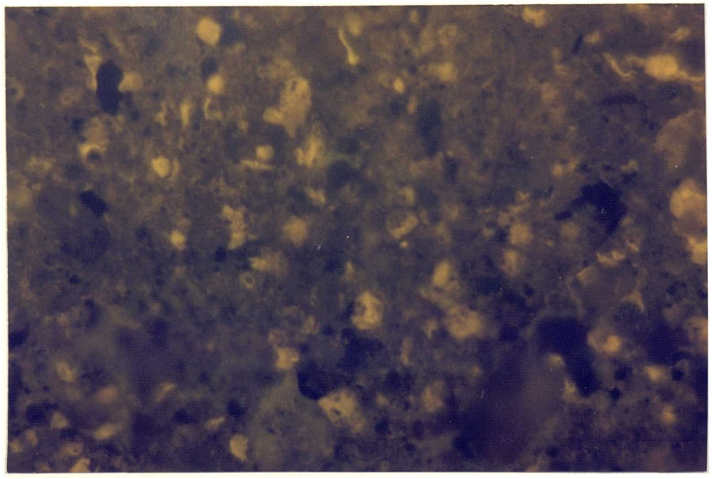


Plate 4.64 Same sample as above cut parallel to bedding: blue-light excitation, oil immersion.

x750



have shown that this texture best develops in vitrinites lying within a restricted rank range (%R_ov≈0.8-1.3) which have been subjected to rapid heating. In the geological environment the heat source is provided by igneous activity. The mosaiced material (%$R_o$av=0.77 in the two samples for which reflectance could be determined) in several Queenslie Marine Band samples co-exists with non-mosaiced vitrinite with reflectances less than %$R_o$av=0.60 in samples which do not appear, on the basis of rank-map data (see next chapter), to have achieved this level of maturity by being in close proximity to igneous intrusions. This observation suggests that the finely-mosaiced material is not vitrinitic in composition. A clue to the composition of the mosaiced material is provided by the presence of vacuoles (Plate 4.68) which suggests devolatilisation through heating, even though the vitrinite in the sample is of sub-bituminous rank (%$R_o$av≈0.55). Vacuolation and mosaics have been detected in many bitumens from immature samples in the West Canada Basin in areas where there is not thought to have been any igneous activity (J.M.Jones *personal communication*). This observation therefore suggests that bitumens possess a much lower temperature threshold for mosaic formation than vitrinites and that the temperature increase which occurs with increasing depth of burial may be sufficient to induce the necessary molecular mobility required for mosaic formation in at least some bituminous substances. Apart from the mosaics and vacuoles there is no other evidence of heating of the sample illustrated in Plate 4.68 (QMB74). Unlike many of the samples containing the mosaiced material, QMB74 lies at the edge of a zone in which rank increase *may* be associated with the presence of an underlying igneous mass (see Chapter 5). It is therefore difficult to assess whether the mosaics and vacuolation in this sample are due solely to the background geothermal gradient or whether the sample has received an additional, more rapid heat pulse from a nearby igneous mass which may have been sufficient to mobilise the bituminous matter, but insufficient to cause any changes in the humic macerals. Since, as indicated above, many low-rank samples containing mosaiced matter also lie outside of any igneous influence, it seems likely that most, if not all, of the mosaics in the Queenslie Marine Band were formed during "normal" coalification, i.e. by the heat flow associated with the background geothermal gradient. It is possible that any additional sources of heat may have induced the rapid release of volatiles, giving rise to vacuolation, although this phenomenon was only recorded in one sample. To summarise, the morphological characteristics of material of the type shown in Plates 4.68 and 4.69, i.e. its diffuse and wispy nature, the presence of mosaic textures and the occurrence of these mosaiced moieties in immature samples, are all features which militate for the material being bitumen, or at least

Plate 4.65 Tasmanitid-like algal body in Queenslie Marine Band: blue-light excitation, air.

Dalmacoulter 4 Borehole, Central Coalfield; sample QMB 74.

x750

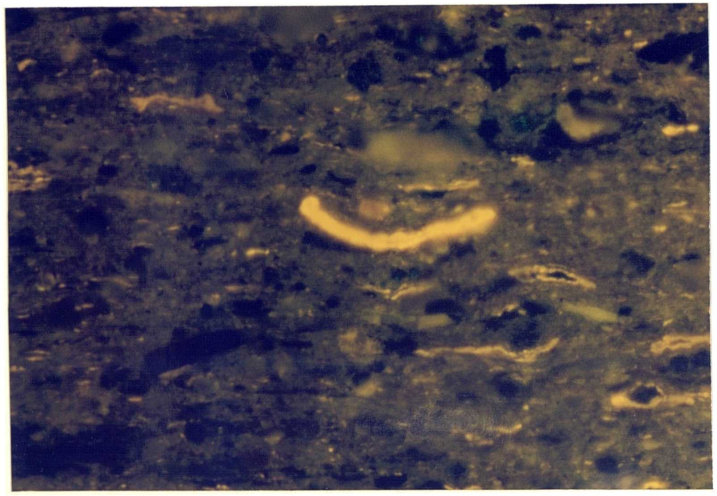


Plate 4.66 Marl lithology of Queenslie Marine Band: reflected light, oil immersion, polarised light.

Bellshill-Newharthill Tower Bore 8/2, Central Coalfield; sample QMB 64.

x750

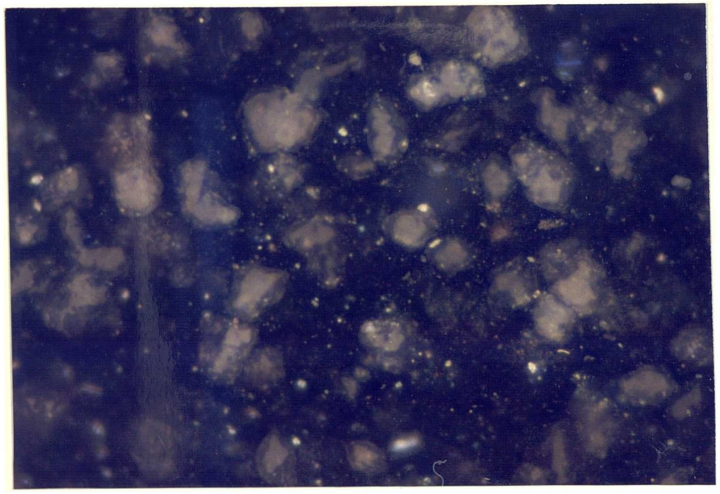
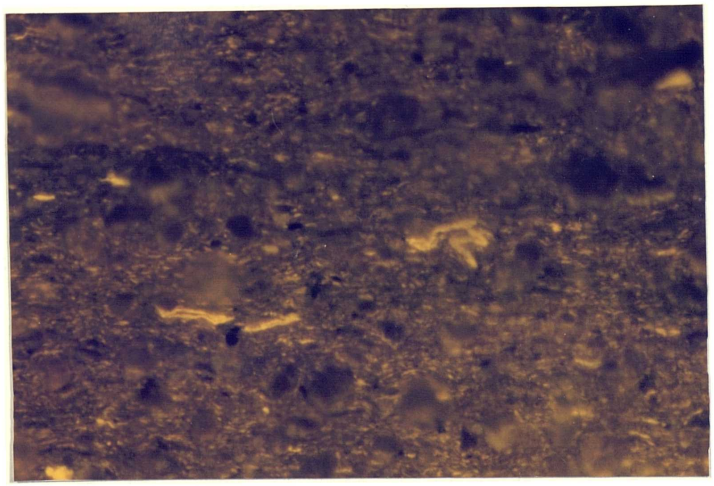


Plate 4.67 Same sample as above showing liptodetrinite flecks and discrete lamalginite wisps: blue-light excitation, air.

x750



bituminous. The increase in temperature experienced during "normal" coalification was probably sufficient to induce mobilisation of the bitumen and the subsequent formation of a fine granular mosaic texture.

The lithological variation observed within the Queenslie Marine Band is sufficiently distinct to enable the construction of a lithological facies map (Fig.4.1). Considerably fewer samples are included in this map than were actually analysed since many samples were from the same borehole or were from localities which were too closely spaced to enable them to be plotted on a map of this scale. Comparison of this map with the faunal map of Brand (Fig.4.2) reveals a broad similarity in the alignment of the different facies. Brand's map is based on the recognition of a number of geographically-distinct faunal communities, each reflecting a given distance from the contemporaneous shoreline and influenced by factors such as bottom conditions, sediment supply and salinity. The areal extent of the *Lingula*-containing facies corresponds well with the area covered by the calcareous samples described in the current study, although Brand (1977) noted that many of the samples within the *Lingula* facies were pyritic in hand specimen. The position of the pyritic facies correlates reasonably well with the localition of the Productoid (aerated marginal environment) facies in the Fife-Midlothian Basin, but correlation of the former with a faunal facies in the Central Coalfield Basin is less distinct. Partial overlap of the pyritic-shale field with the *Myalina* (marginal environment) facies occurs within the southern end of the Central Coalfield Basin only.

The most salient similarity between the two maps is the correspondence between the positions of the Pectinoid/Cephalopod facies and the facies comprising samples containing the mosaiced, bituminous material. The fossils in the former are reported to occur within pyritous mudstones (Brand 1977), this observation concurring with the sample descriptions derived from reflected-light microscopy. From its goniatite content, the Pectinoid/Cephalopod facies is thought to represent the presence of relatively deep water. The restricted occurrence of the bituminous matter and its presence within an area which was probably the deepest part of the depositional basin during Queenslie Marine Band times suggests either that optimum environmental conditions prevailed, favouring the preservation of the bituminous material, or that the mosaiced matter represents the remains of an organism that was confined to the deep-water facies. That the latter alternative may be more apposite is inferred from the frequent association of mosaiced matter with low-reflecting, non-mosaiced areas (see centre of bituminous matter in Plate 4.69 and material below the mosaiced "splodge" in Plate 4.68). Similarly low-reflecting fragments are not uncommonly seen juxtaposed with animal debris such as fish scales, bones and spines, an observation made in many algal-rich

Plate 4.68 Bituminous matter in Queenslie Marine Band showing fine granular mosaic texture and vacuoles. Lower-reflecting, non-mosaiced material occurs below: reflected light, oil immersion, plane-polarised light.

Dalmacoulter 4 Borehole, Central Coalfield; sample QMB 74.

x750

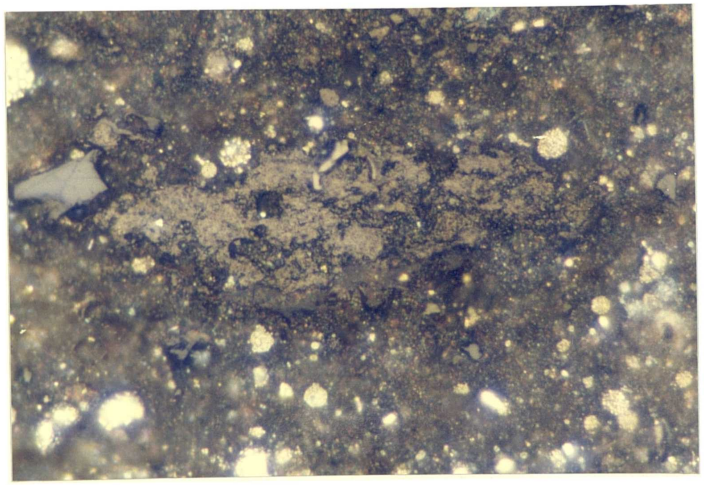


Plate 4.69 Particle of finely-mosaiced matter incorporating non-mosaiced, low-reflecting shard: reflected light, oil immersion, plane-polarised light.

Dalmacoulter 2 borehole, Central Coalfield; sample QMB 46.

x750

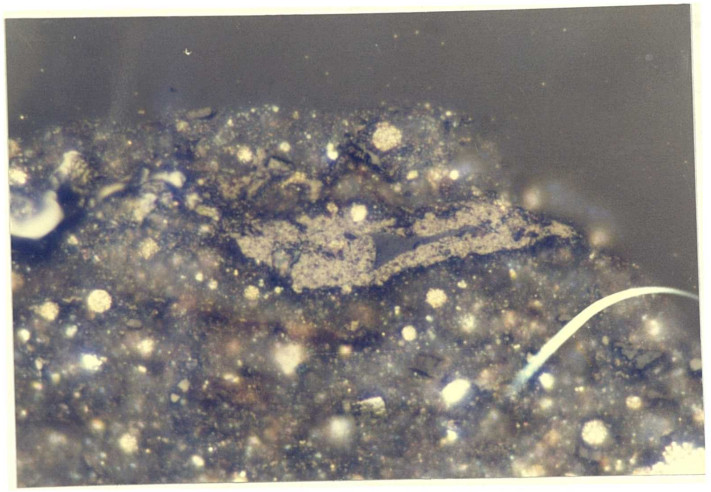
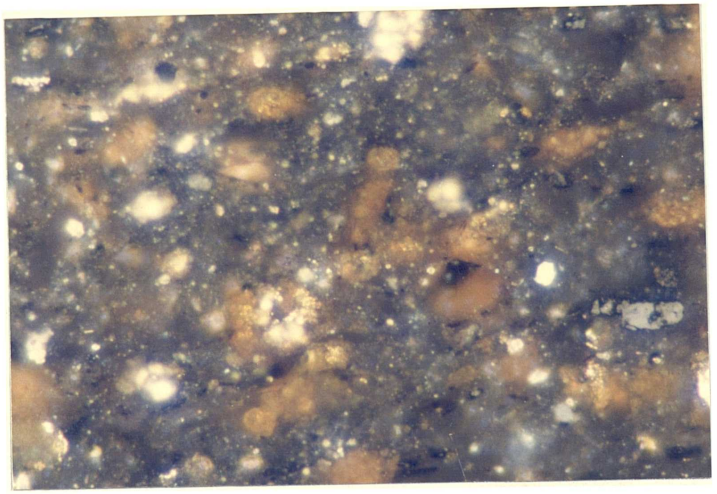


Plate 4.70 Pyritic shale showing alteration of pyrite to ion oxides (orange): reflected light,oil immersion, plane-polarised light.

Firth of Forth Tower Bore 2, Fife-Midlothian Basin; sample QMB A2.

x750



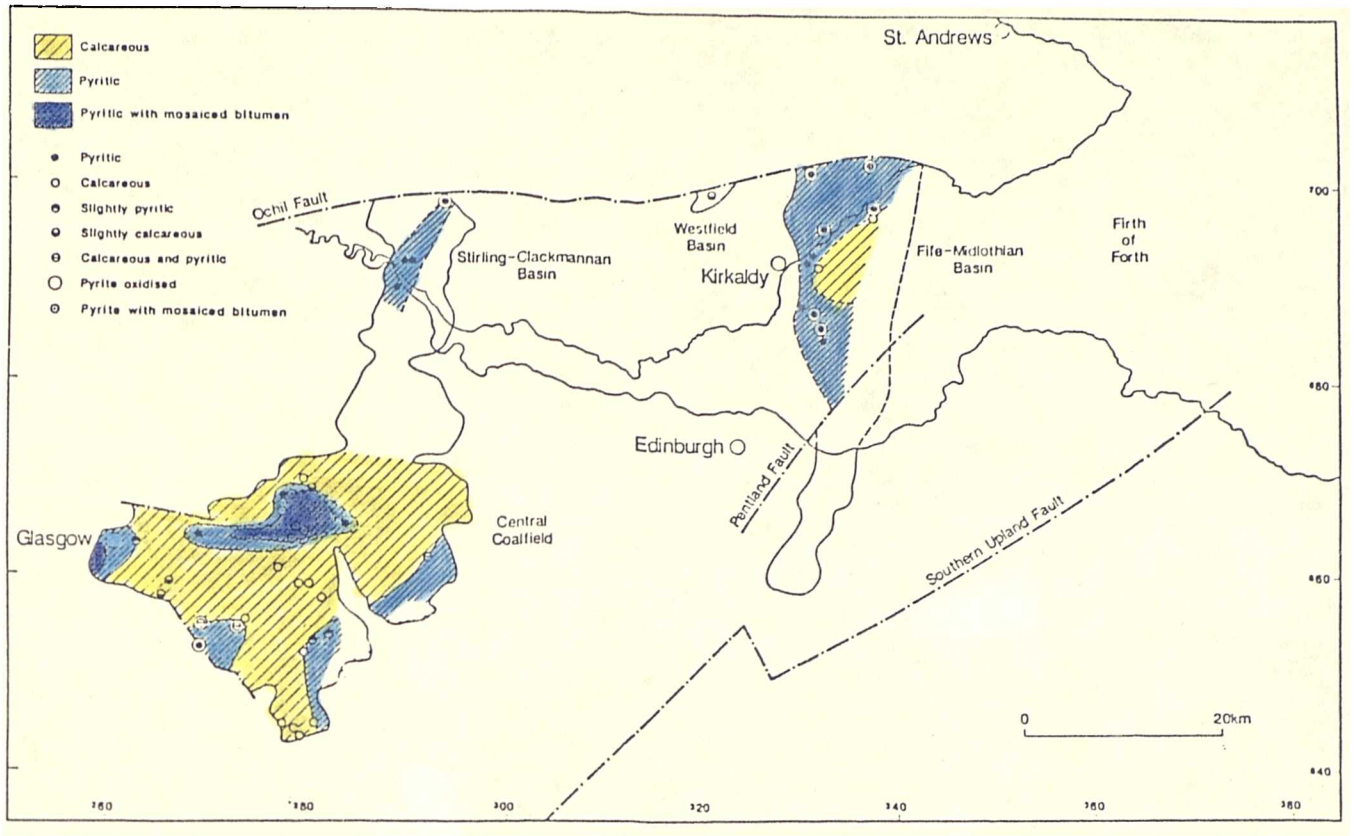


Fig.4.1 Facies map of the Queenslie Marine Band.

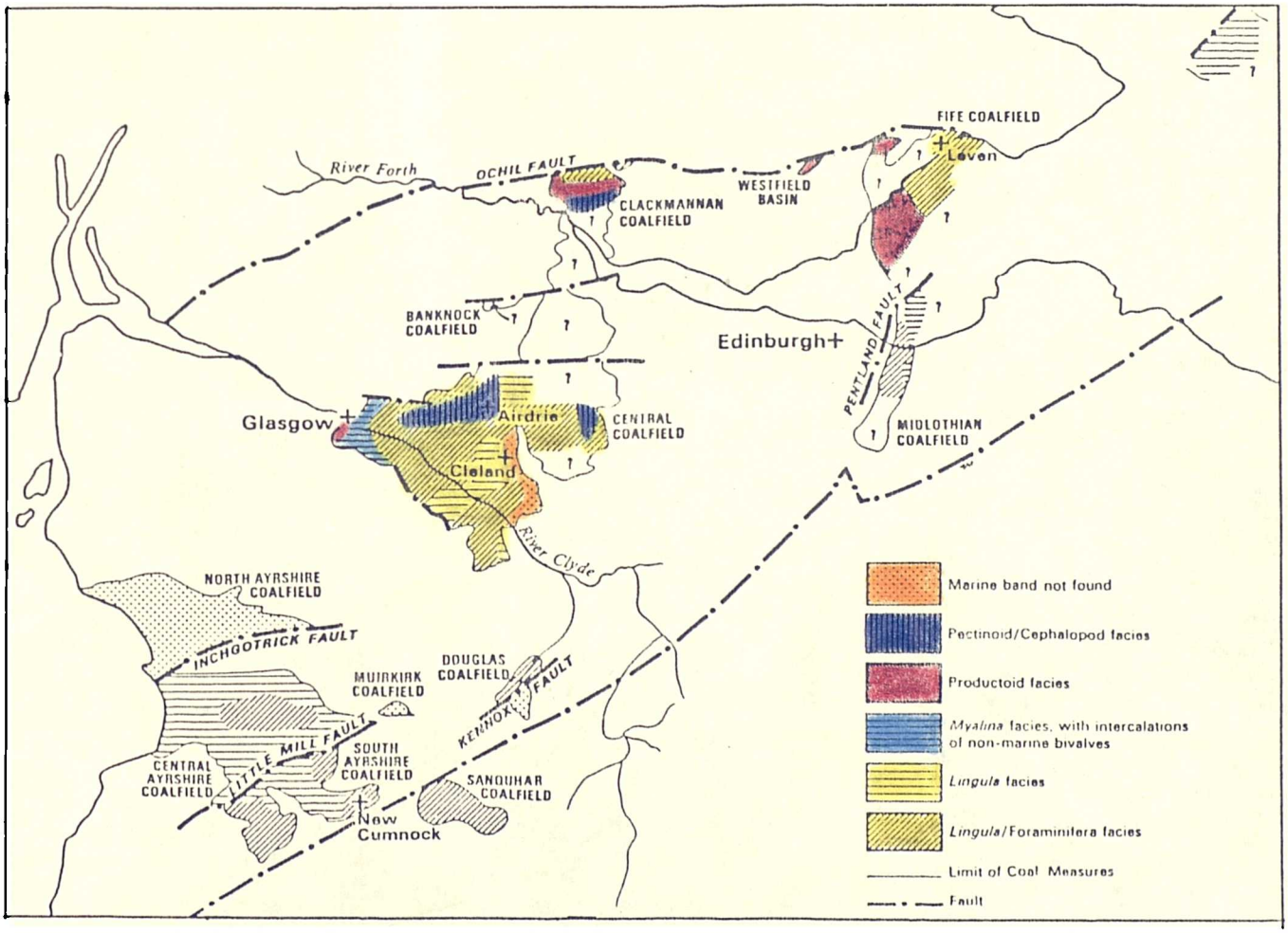


Fig.4.2 Distribution of faunal facies in the Queenslie Marine Band (modified from Brand 1977).

deposits. It is therefore possible that the wispy bituminous matter represents the remains of the soft (?more thermally-labile) parts of some unknown organism.

It is apparent from the foregoing account that, although a broad correlation can be recognised between the locations of the lithological and palaeontological facies, by comparing Figs 4.1 and 4.2, reflected-light microscopy appears less sensitive in detecting variations in depositional environments within the Queenslie Marine Band than the traditional palaeontological methods.

A further feature which deserves comment is the partial or complete oxidation of pyrite in many Queenslie Marine Band samples. The pyrite may have altered to orange-coloured iron oxides (Plate 4.70) or to haematite. In some samples, oxidation may be sufficiently severe to cause reddening of the rock matrix and oxidation of phytoclasts. The oxidation phenomenon is particularly noticeable in samples from the Fife-Midlothian Basin (see Fig.4.1). Irregular reddening of Coal Measures strata in the Upper and Middle Coal Measures of the Fife Coalfield Basins has long been recognised (Francis and Ewing 1962) and, as with the reddening of strata noted in the Ayrshire Coalfield (Mykura 1960), is thought to be due to the downward percolation of oxidising solutions related to the development of a Permian unconformity, although Permian sediments are not recognised in Fife. The occurrence of red beds in Lower Coal Measures strata is less well documented, but they have been reported in strata within the Leven Syncline (Francis and Ewing 1962). That all of the pyrite-altered Queenslie Marine Band samples analysed were not red in hand specimen illustrates the sensitivity of reflected-light microscopy in detecting the oxidation phenomenon. Since the Queenslie Marine Band lies at the base of the Middle Coal Measures, the occurrence throughout the Fife-Midlothian Basin of samples containing oxidised pyrite suggests that the extension of post-Carboniferous weathering into the Lower Coal Measures may have occurred over a more geographically widespread area than previously supposed.

The percolation of oxidising solutions down fault planes has been invoked to explain major areas of reddened strata found adjacent to many faults within the Ayrshire Basin (Mykura 1960). It is therefore feasible that the fault-controlled movement of oxidising solutions could have contributed to the oxidation of pyrite within some samples lying near the major faults in the eastern and central Midland Valley coalfield basins (Fig.4.1).

4.2.3.2 Calmy Blaes

The marine shales associated with the Calmy Limestone (Upper Limestone Group) are termed the Calmy Blaes and are prefixed "C" in the sample descriptions given in the Appendix.

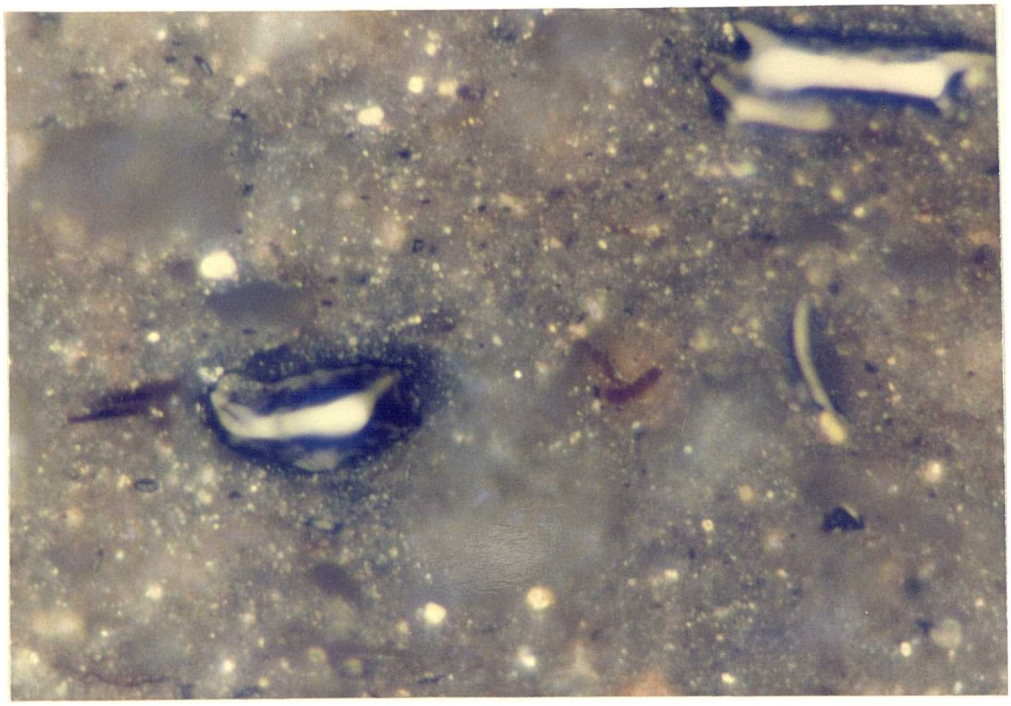


Plate 4.71 Typical field of view in non-pyritic sample from the Calmy Blaes. Brown entities in the centre are spore fragments: reflected light, oil immersion, plane-polarised light.

Meggie Den Bore, east Fife; sample C 3.

x750

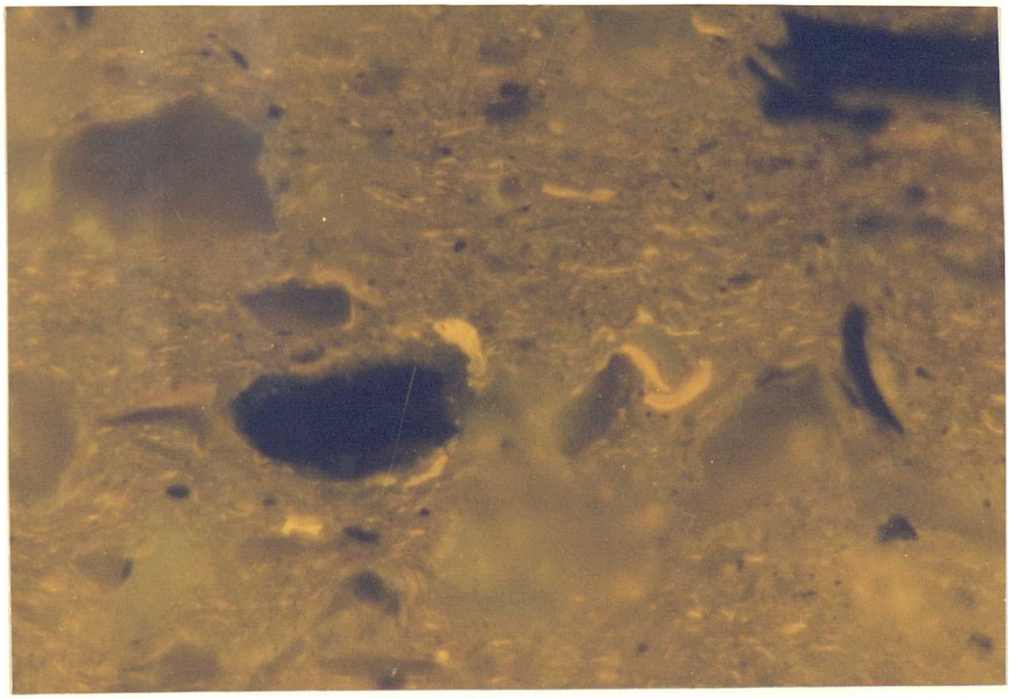


Plate 4.72 Same field of view as above showing matrix filled mainly with liptodetrinite flecks: blue-light excitation, oil immersion.

x750

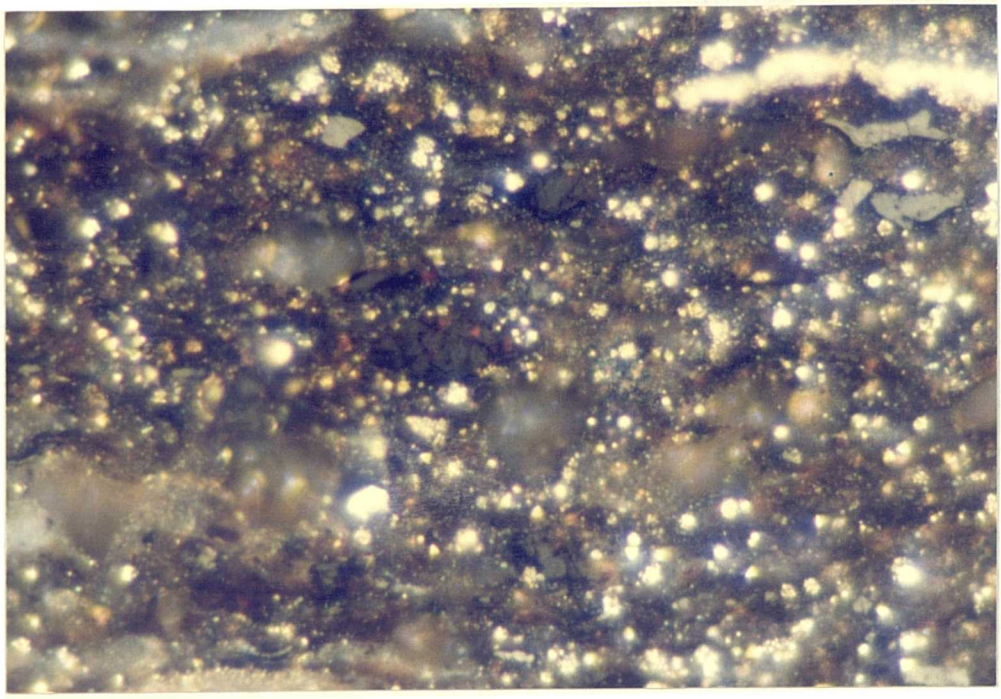


Plate 4.73 Pyritic, organic-rich shale sample from the Calmy Blaes: reflected light, oil immersion, plane-polarised light.

Cattlemoss Bore, west Fife; sample C 82.

x750

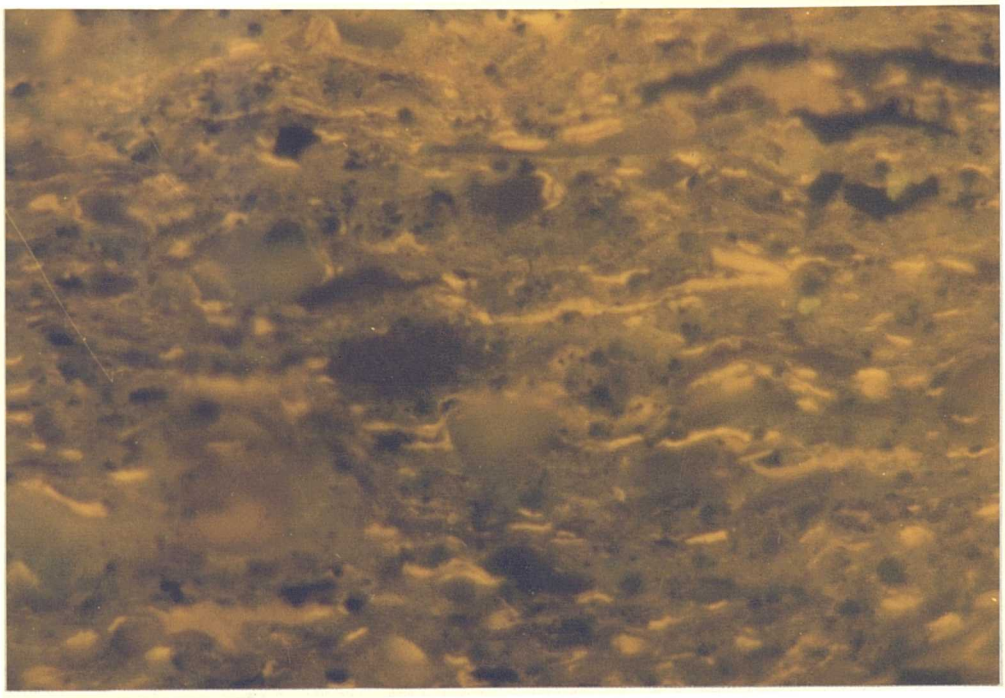


Plate 4.74 Same field of view as above showing discrete, short, lamalginite wisps: blue-light excitation, oil immersion.

x750

The shales comprising the Calmy Blaes may contain varying amounts of calcite, pyrite or silty material. Their organic content is variable, ranging from low to very high. In samples whose liptinitic content is less than c.30% of the total organic matter (e.g. Plate 4.71), inertinite fragments dominate the maceral assemblages, and vitrinite is present in relatively small amounts (usually less than c.5% of the total organic matter present). The liptinite assemblage in this type of sample comprises mainly spore fragments and liptodetrinite flecks (e.g. Plate 4.72). The pyritic shales contain the highest amounts of organic matter (Plates 4.73 and 4.74). High liptinite contents (>50% of the total organic matter) are also associated with the pyritic shales, in which the proportion of vitrinite is also seen to increase (c.10-30% of the total organic content).

In liptinite-rich samples, the principal maceral is discrete lamalginite. The maceral occurs either in the form of short, discrete entities (c.10-30µm long: Plate 4.74) which, in sections parallel to bedding, have a cyst-like habit (see Plate 4.64) or it occurs as long filaments, these being thicker than those in lamosites. The filamentous algae in the Calmy shales (Plate 4.75) are c.2-3µm wide and are generally in the order of 50-100µm in length. These longer types of filament can mat together, imparting a distinct banded appearance to the rock when observed in reflected light. The discrete lamalginite invariably occurs with sporinite and amorphous material: it is never seen in association with liptodetrinite flecks of the kind dominating the maceral assemblage shown in Plate 4.72. The discrete lamalginite and liptodetrinite therefore appear to be mutually exclusive. The amorphous material probably derives from degraded algal remains and may impregnate the mineral groundmass, leading to a background matrix fluorescence when viewed under blue-light excitation. Matrix impregnation is not thought to be severe since a heavy matrix stain is not observed in reflected light (Plates 4.76 and 4.77). Small quantities of *Botryococcus* (≤5% of the total maceral assemblage) may occur within both the liptodetrinite-dominated and lamalginite-dominated assemblages.

4.2.3.3 Index Blaes

The shales associated with the Index Limestone (Upper Limestone Group; prefixed "I" in the Appendix) have no particularly distinctive petrographic characteristics. The lithology is shale which may be calcareous, silty or pyritic, usually with a moderate to high organic content. The matrix stain is generally light overall, but is darkened by abundant flecks of bituminous matter.

Inertinite fragments dominate the maceral assemblage in most samples. The vitrinite content does not normally exceed 10% of the total organic matter, and

Plate 4.75 Sample from Calmy Blaes showing long, discrete lamalginite and shorter wisps. Matting of filaments leads to the development of thicker bands: blue-light excitation, air.

Gartarry Toll Borehole; sample GAR 18.

x750

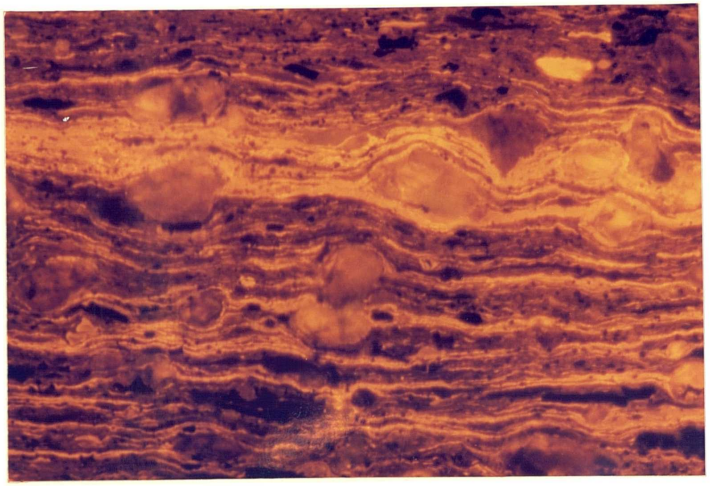


Plate 4.76 Pyritic sample from the Calmy Blaes displaying light overall staining of the mineral groundmass: reflected light, oil immersion, plane-polarised light.

Gartarry Toll Borehole; sample GAR 18.

x750

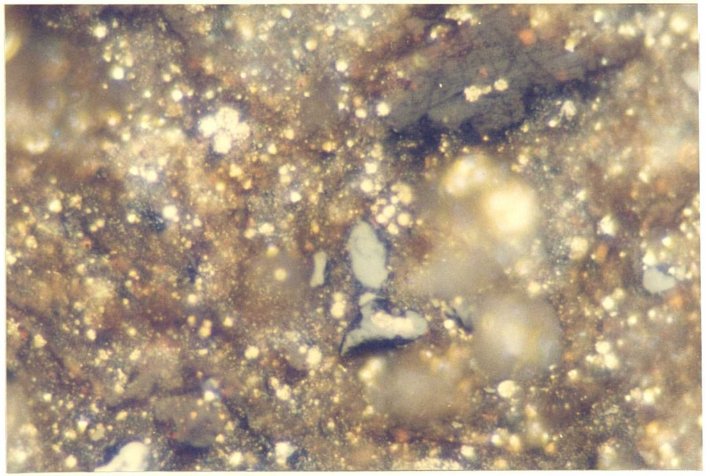
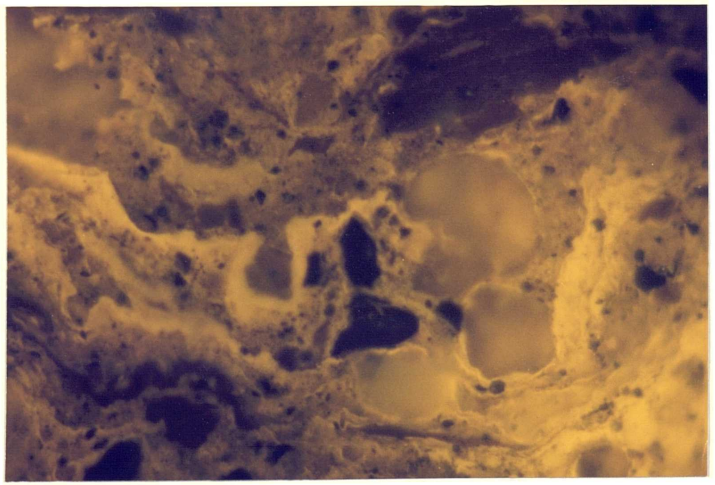


Plate 4.77 Same field of view as above showing amorphous matter (probably degraded lamalginite) impregnating the mineral groundmass: blue-light excitation, oil immersion.

x750



the liptinite content does not usually exceed 20%. The liptinite fraction comprises liptodetrinite and sporinite fragments, in roughly equal amounts, the former displaying a moderate rather than an intense fluorescence intensity suggesting a non-algal origin. The liptodetrinite is finely dispersed throughout the mineral matrix.

4.2.3.4 Kelty Blackband = Kelty *Lingula* Band

The samples analysed from the Kelty Blackband (Limestone Coal Group; prefixed "KBBI" in the Appendix) were mainly shales with varying amounts of pyrite and/or calcite. The organic content of the shales is invariably high with the bulk of the organic matter comprising vascular-plant debris (Plates 4.78-4.81). The organic content is sufficiently high for some samples to be classed as carbargilites.

The liptinite fraction dominates the maceral assemblage, frequently accounting for over 50% of the total organic content. Sporinite in varying degress of preservation (Plate 4.79) constitutes much of the liptinite fraction although liptodetrinite wisps and flecks (Plate 4.81) may also comprise a significant part of the hydrogen-prone matter, usually within the more calcareous samples. The liptodetrinite in Kelty Blackband samples displays variable fluorescence intensities and colours which suggests that it is of mixed origin. The intense, yellow fluorescence displayed by many of the flecks, akin to that observed in liptodetrinite within the Queenslie Marine Band, suggests an algal origin, while the duller, more orange fluorescence, particularly of the wispier entities, is more consistent with an origin from terrestrial organic matter (probably sporinite).

Remains of *Botryococcus braunii* are common within the Kelty Blackband. They are particularly abundant in carbargilitic sediments which are very finely laminated and which have a similar appearance to cannel coals (Plate 4.82). Unlike *Botryococcus* in the torbanitic deposits, those in the finely-laminated Kelty Blackband samples are elliptical in sections perpendicular to bedding which suggests that the algae have been compressed. A contribution to the organic matter from tasmanitid-derived telalginite is inferred in some samples by the occurrence of very intensely fluorescing yellow fragments, some of which bear a morphological resemblance to *Tasmanites* (see arrowed fragment in Plate 4.81).

The very heavy bitumen staining of the mineral matrix observed in many Kelty Blackband samples is a consequence of their high liptinite content. That the dark material which appears to be saturating the mineral matrix in several samples (e.g. Plate 4.80) is hydrogen-prone is indicated by the moderate to dull matrix fluorescence of these samples, a phenomenon not necessarily accompanied

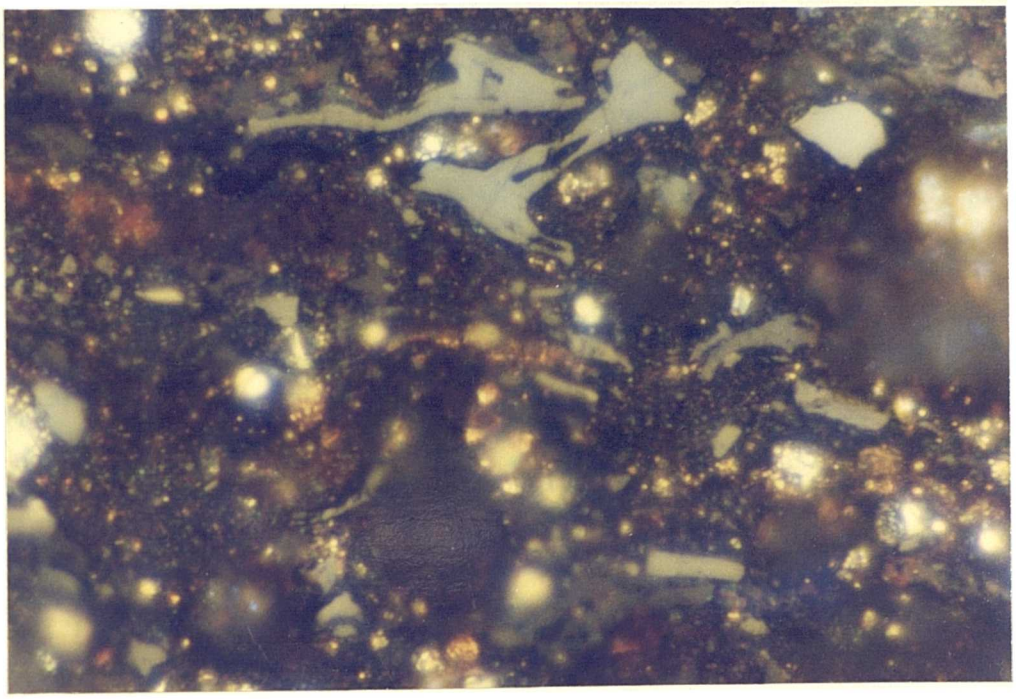


Plate 4.78 Typical field of view of a Kelty Blackband sample in which the organic-matter assemblage is dominated by vascular-plant debris: reflected light, oil immersion, plane-polarised light.

Cartmore 2 Bore, central Fife; sample KBBI 547/2.

x750

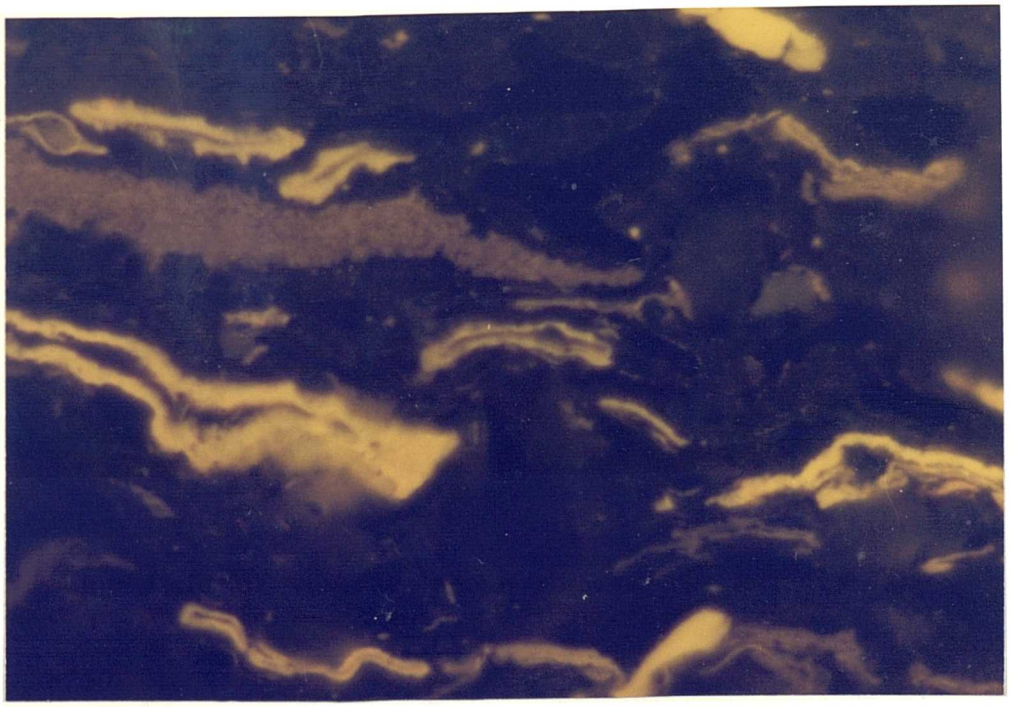


Plate 4.79 Same field of view as above showing sporinite in varying degrees of preservation: blue-light excitation, oil immersion.

x750

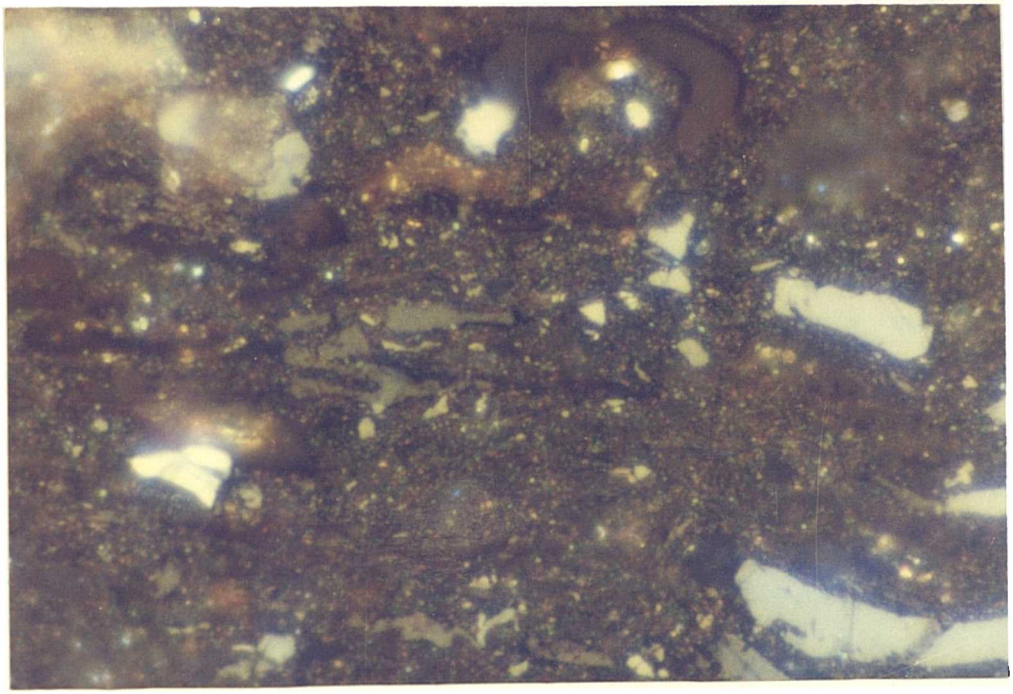


Plate 4.80 Sample of Kelty Blackband Ironstone showing saturation of sedimentary matrix with bituminous matter: reflected light, oil immersion, plane-polarised light.

Westerton 116 Bore, central Fife; sample KBBI 185.

x750

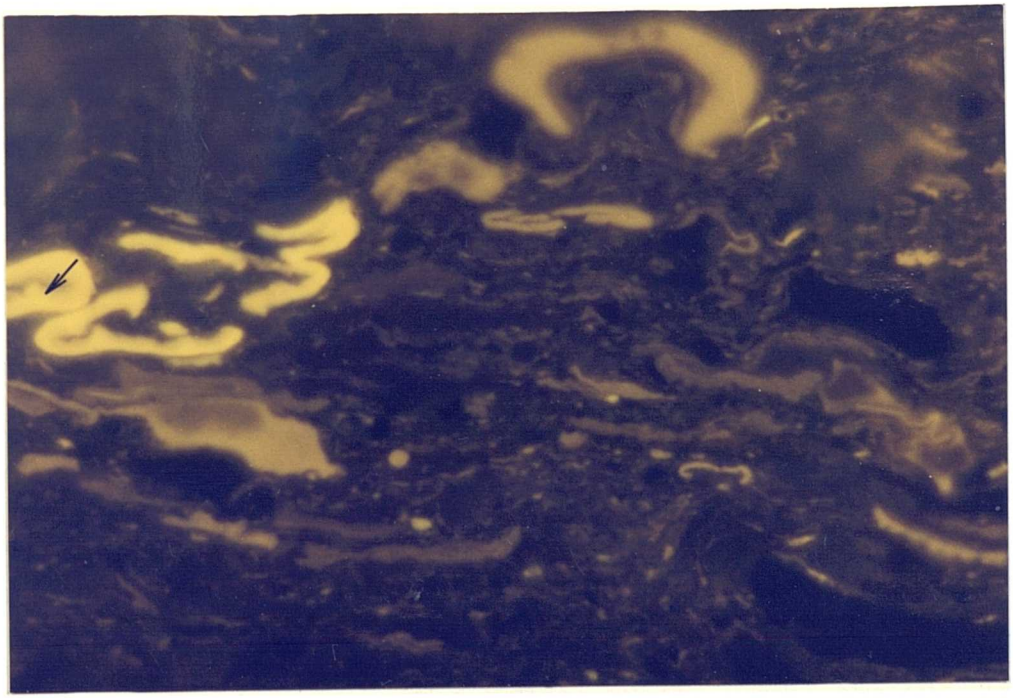


Plate 4.81 Same field of view as above showing abundant thick- and thin-walled spore debris and matrix filled with liptodetrinite. Intensely-fluorescing, yellow fragments are probably tasmanitid algae: blue-light excitation, oil immersion.

x750

by the presence of a dark mineral matrix. A further feature which is particularly marked in Kelty Blackband samples, and again reflects their high content of hydrogen-prone matter, is the severe clouding of the immersion oil observed during fluorescence microscopy. The clouding arises through the dissolving of hydrocarbons in the sample by immersion oil, and the process is enhanced by the heat generated during blue-light excitation. Hydrocarbon generation is sometimes sufficiently severe to cause blooming of air objectives.

Although termed Kelty Blackband, suggesting a close association with iron carbonate (MacGregor 1920), no reddening or banding was observed in the hand specimens and no iron mineralisation greater than what might normally have been expected, i.e. the occasional "blotch", was detected during reflected-light examination of any of the Kelty Blackband samples investigated. This situation is in marked contrast to that of miscellaneous banded blackband samples described in the Appendix (p.241) which contain abundant stringers and lenses of siderite. The iron carbonate may also be finely disseminated throughout the mineral matrix (Plate 4.83). As in the Kelty Blackband, the liptinite assemblage of the "true" blackbands is dominated by sporinite, but liptodetrinite and *Botryococcus* can be major constituents as illustrated by a sample of the Lochgelly Blackband (Plate 4.84) which, along with the Kelty Blackband, is an important marker horizon within the Limestone Coal Group in Fife.

4.2.3.5 Black Metals Marine Band

The Black Metals Marine Band represents the upper of two principal marine incursions that occur within the Limestone Coal Group (p.27). The samples investigated are prefixed "BM" in the Appendix.

Akin to the Kelty Blackband, the shales of the Black Metals Marine Band may be silty, calcareous or pyritic and their organic content is invariably high. Inertinite is generally the main organic component (usually >50% of the total organic matter present) with vitrinite normally accounting for between c.5-20% of the total organic assemblage. Liptinite does not in general comprise more than 20% of the organic matter and, consequently, the overall staining of the sedimentary matrix in Black Metals samples is light. Increasing liptinite content is usually accompanied by a darkening of the mineral groundmass.

The liptinite fraction consists mainly of sporinite, largely in the form of thin-walled spores, which are highly fragmented and often degraded, so giving rise to the diffuse outlines seen in some sections (Plate 4.85). Liptodetrinite is dispersed within many Black Metal samples (Plate 4.85), but rarely accounts for more than 10% of the total organic matter present. The liptodetrinite displays

Plate 4.82 Finely-laminated, cannel-like sample of Kelty Blackband Ironstone comprising thin-walled spores, liptodetrinite and compressed *Botryococcus* remains: reflected light, air, plane-polarised light.

Kelty 2 Bore, central Fife; sample KBBI 894/2.

x750

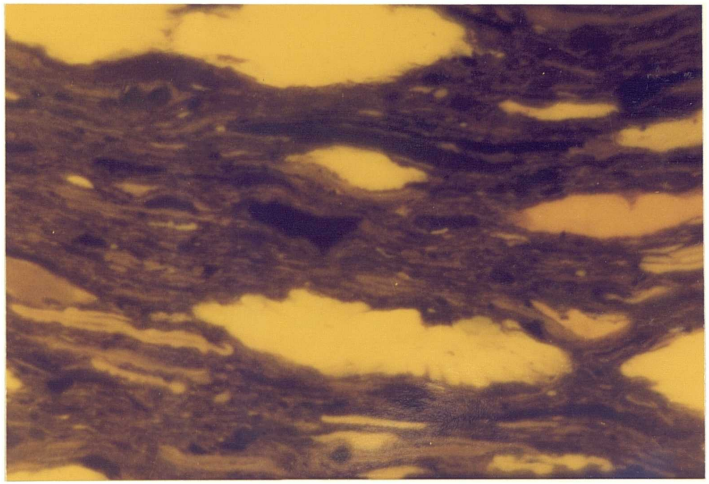


Plate 4.83 Sample of Lochgelly Blackband Ironstone showing the disseminated nature of the carbonate: reflected light, oil immersion.

Sample from BGS bore NT29NW509, central Fife; sample C 3.

x750

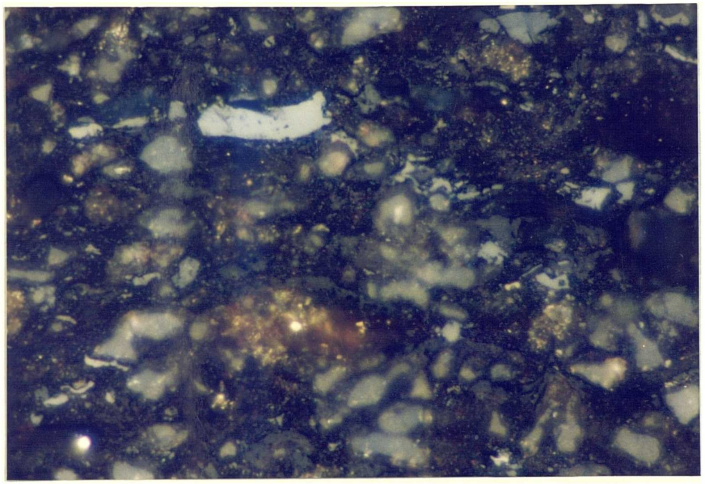
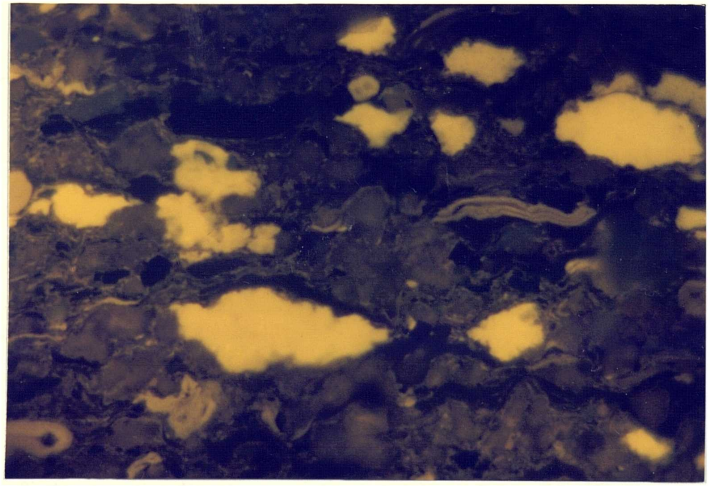


Plate 4.84 Same field of view as above showing remains of *Botryococcus* telalginite, thin-walled spores and liptodetrinite. Left-hand field of view exposed to blue-light irradiation for several minutes: blue-light excitation, oil immersion.

x750



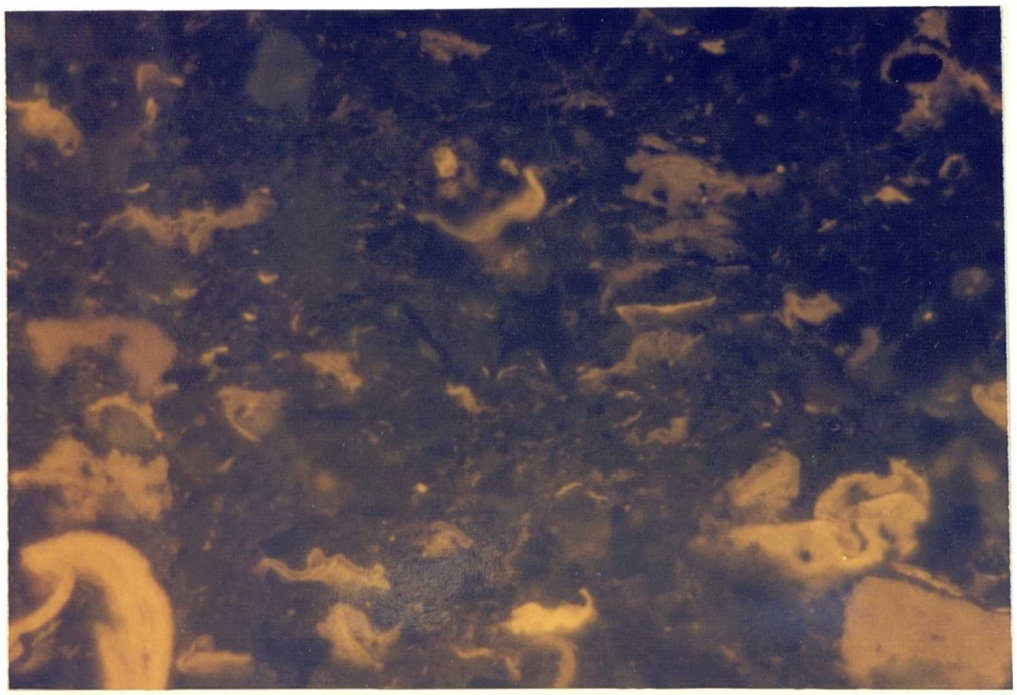


Plate 4.85 Typical liptinite assemblage within the Black Metals Marine Band showing degraded spore debris and flecks of liptodetrinite: blue-light excitation, oil immersion.

Highholm 74 Bore, west Fife; sample BM 806a.

x750

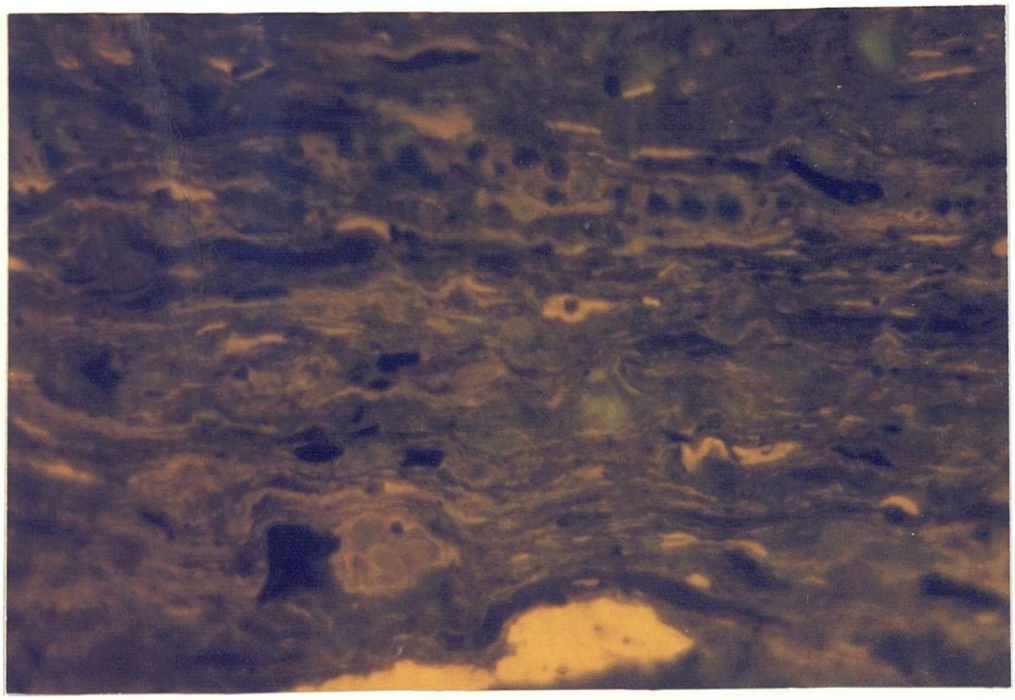


Plate 4.86 Typical algal-rich assemblage in the Black Metals Marine Band showing diffuse, wispy, discrete lamalginite. Thicker elongate entities are probably spore fragments. *Botryococcus* remains lie at the bottom of the field: blue-light excitation, oil immersion.

Loch Glow Bore, central Fife; sample BM 63.

x750

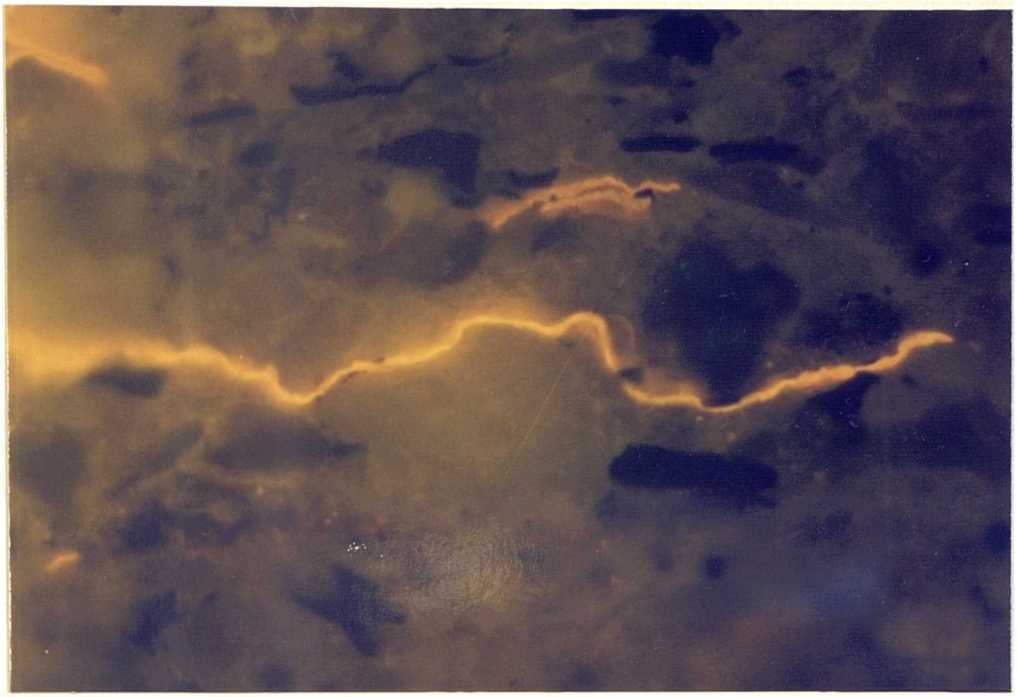


Plate 4.87 Long, filamentous lamalginite which occurs sporadically in the Black Metals Marine Band: blue-light excitation, oil immersion.

Keirsbeath 3 Borehole, central Fife; sample BM 64.

x750

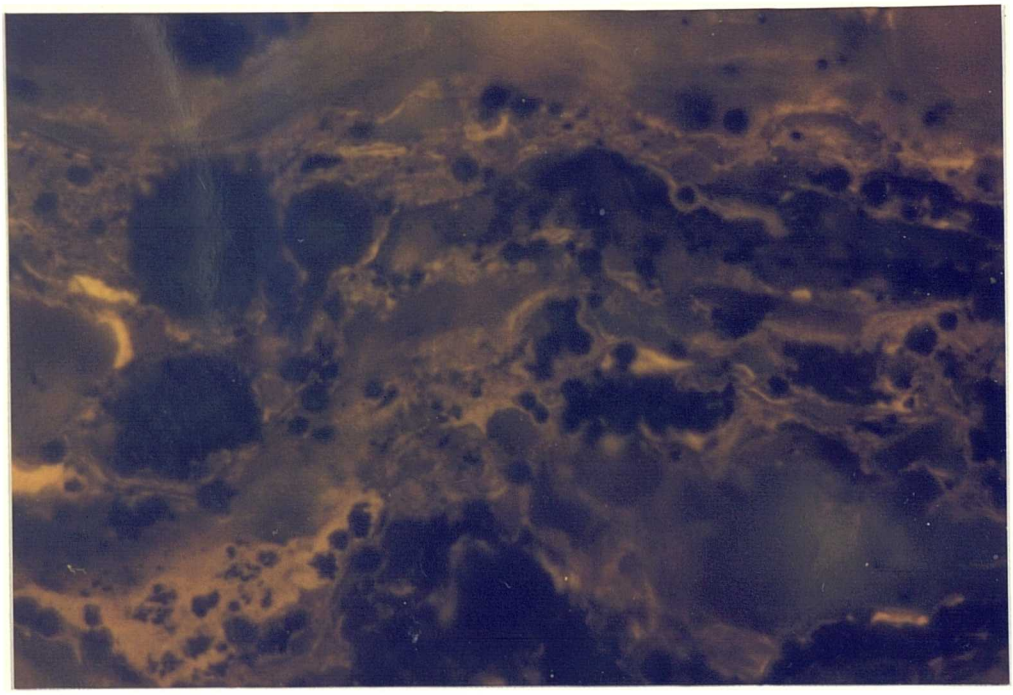


Plate 4.88 Amorphous matter impregnating the mineral matrix which also contains discrete lamalginite: blue-light excitation, oil immersion.

Thornton 34 Bore, central Fife; sample BM 266.

x750

similar fluorescence properties to the terrestrial debris, indicating that it probably represents finely-comminuted fragments of exinitic land-plant material. The liptinite fraction in some Black Metals samples is dominated by discrete wisps of lamalginite which are usually *c.*20-30µm long and, like the sporinite, often display hazy margins, suggesting that they have been partially degraded (Plate 4.86). Longer (*c.*150µm), more intensely-fluorescing algal filaments of the type shown in Plate 4.87 also occur, albeit sporadically, as do traces of *Botryococcus* telalginite. Samples in which liptinite represents more than 30% of the total organic matter present sometimes have mineral matrices impregnated with moderate- to intensely-fluorescing amorphous matter (Plate 4.88). The current petrological investigations did not confirm whether the material represents the degraded remains of algae or spores. Although the partial degradation of organic matter may account for the indistinct appearance of some of the exinitic matter in Plates 4.85, 4.86 and 4.88, clouding of the immersion oil, referred to in the previous section, probably also contributes to the haziness evident in these photomicrographs.

4.2.3.6 Johnstone Shell Bed

This horizon occurs near the base of the Limestone Coal Group and represents the lower major marine incursion within this stratigraphic interval. Samples from this horizon are prefixed "JSB" in the Appendix.

The lithological character of the Johnstone Shell Bed is similar to that of the Black Metals Marine Band and the organic content is similarly high (Plates 4.89 and 4.90). The dominance of inertinitic debris is not as pronounced within the Johnstone Shell Bed as in the Black Metals, since the proportion of liptinite and vitrinite in the Johnstone Shell Bed is higher. Vitrinite comprises approximately 10-30% of the total organic matter present, whilst liptinitic components represent *c.*20-50%. The thin-walled spores account for most of the liptinite and, like the spores in the Black Metals, they are fragmented and often degraded. In contrast to the Black Metals, liptodetrinite in the Johnstone Shell Bed is much less widespread and discrete lamalginite wisps and long algal filaments are rare. The presence in some samples of intensely-fluorescing,yellow , thin-walled entities, for example, those in the centre of Plate 4.91, probably reflects a contribution from *Tasmanites* telalginite.

4.2.3.7 Charlestown Main Limestone Horizon

Only eighteen samples from shales closely associated with the Charlestown Main Limestone (Lower Limestone Group) and its correlatives (Seafield Tower and

Plate 4.89 Typical appearance of a sample of the Johnstone Shell Bed showing high organic content and moderate to dark overall bitumen staining of the mineral matrix: reflected light, oil immersion, plane-polarised light.

Bowhill 360Fm Mine, central Fife; sample JSB 334.

x750

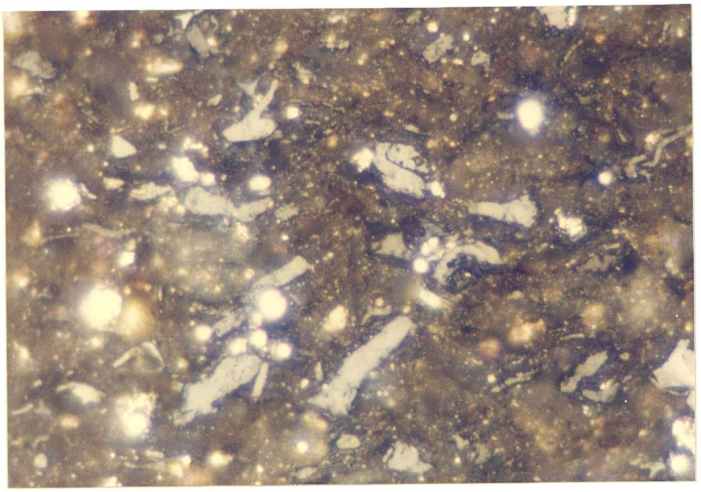


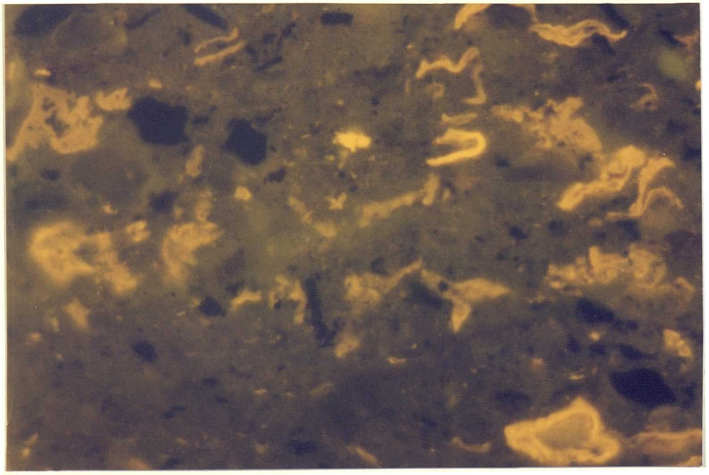
Plate 4.90 Same field of view as above showing thin-walled microspores: blue-light excitation, oil immersion.

x750

Plate 4.91 Degraded spore material with intensely-fluorescing, yellow, probable tasmanitid fragments in the centre of the plate: blue-light excitation, oil immersion.

Whitefield Road 1 Bore, central Fife; sample JSB 289.

x750



3rd Abden Limestones) were available for analysis. Severe thermal alteration of eleven of these samples by the closely-underlying Midland Valley Sill prevented an accurate appraisal of organic-matter variation within this stratigraphic interval. Of the few remaining non-heat-affected samples in which macerals could be distinguished, the organic assemblages did not appear to be particularly distinctive.

The organic content of the shales (often silty and calcareous) was generally low to moderate and the overall matrix staining was light to moderate. As in most of the sediments discussed so far, inertinite comprised the greatest fraction of the organic matter present (>50%). The vitrinite content was variable (trace amounts up to 30%), and liptinite constituted up to 30% of the total organic content. The liptinite fraction was represented by thin-walled microspore fragments, liptodetrinite flecks of unknown affinity and *Botryococcus* fragments.

4.2.3.8 Miscellaneous

This section describes other types and assemblages of organic matter occurring in argillaceous sediments which, from palaeontological evidence in records provided by the British Geological Survey, are known to have been deposited in marine environments.

Despite being of marine provenance, the samples shown in Plates 4.92 to 4.94 contain substantial amounts of vitrinite and inertinite. The thick-walled, intensely-fluorescing yellow body in the centre of Plate 4.93 represents the remains of *Tasmanites* and is the best example of this alga recorded in sediments from the Midland Valley. In addition to its high fluorescence intensity, the prismatic structures visible within the cell wall under reflected light (Plate 4.92) are diagnostic features of this marine alga. The morphology of this telalginite is very similar to that documented for *Tasmanites* occurring within many tasmanitid-rich deposits in other parts of the world (Hutton *et al.* 1980; Cook *et al.* 1981). A major difference is that the Midland Valley tasmanitids are very small (*c.*30-50μm in length) whereas those documented in other *Tasmanite*-containing shales are usually *c.*200μm in length.

Degraded organic debris with a similar fluorescence colour and intensity to the *Tasmanites* in Plate 4.93 is found in a marine sample shown in Plate 4.94. Although the thick-walled nature of the *Tasmanites* cyst is not apparent in Plate 4.94, this intensely-fluorescing material could be *Tasmanites* remains since tasmanitid telalginite can also occur in the form of thin, "stringy" filaments. At least some of these filamentous structures are thought to originate through detachment of the discrete membranous layers of which the whole, thick, algal cyst is composed (A.C.Cook *personal communication*).

Plate 4.92 Marine shale showing thick-walled *Tasmanites* with characteristic internal prismatic structure: reflected light, oil immersion, plane-polarised light.

Gartarry Toll Borehole, Passage Group; sample GAR 8.

x750

Plate 4.93 Same field of view as above. Intensely-fluorescing liptodetrinite flecks may, in part, be derived from *Tasmanites*: blue-light excitation, oil immersion.

x750

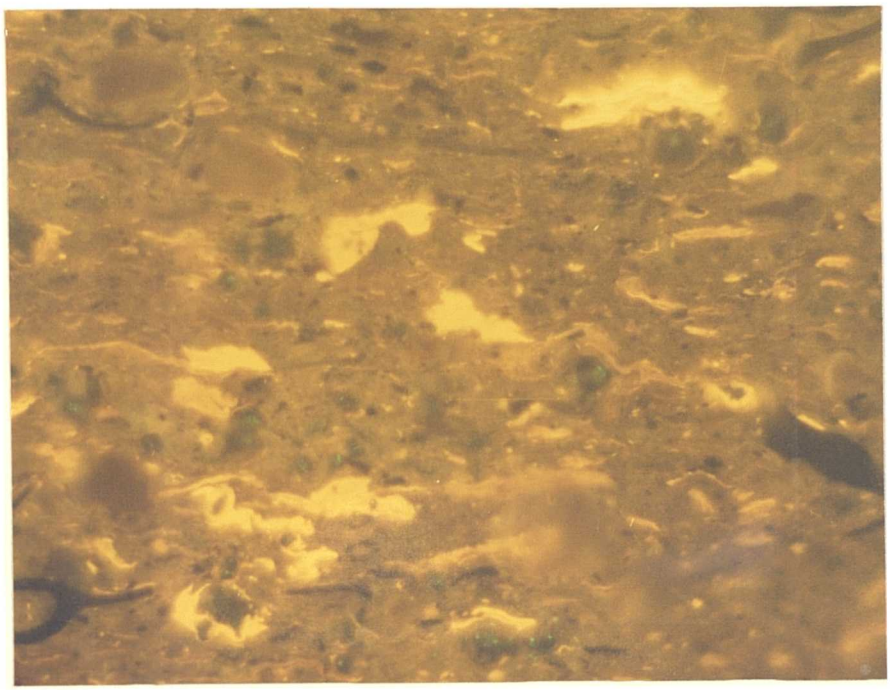


Plate 4.94 Marine shale containing probable degraded thin-walled *Tasmanites* (intensely fluorescing), liptodetrinite flecks and thin-walled microspores (moderately-fluorescing, orange, wispy entities): blue-light excitation, oil immersion.

Gartarry Toll Borehole, Upper Limestone Group; sample GAR 5.

x750

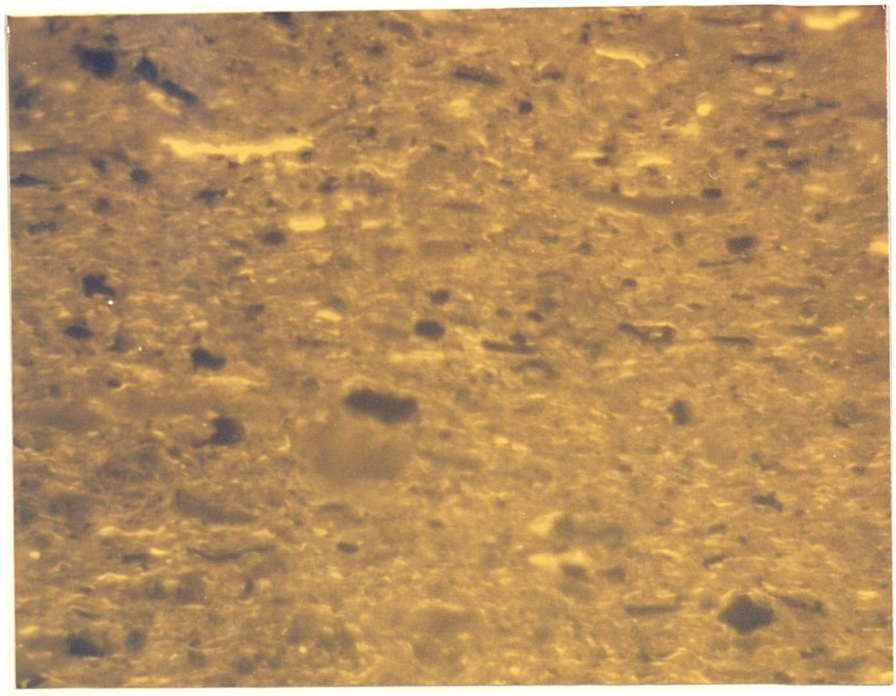


Plate 4.95 Marine shale containing liptodetrinite and probable *Tasmanites* fragments: blue-light excitation, oil immersion.

Gartarry Toll Borehole, Upper Limestone Group; sample GAR15.

x750

Plate 4.96 Marine shale containing probable thick-walled *Tasmanites* and discrete lamalginite, section perpendicular to bedding: blue-light excitation, oil immersion.

Firth of Forth Tower Bore 1, Passage Group; sample FOF 1b

x750

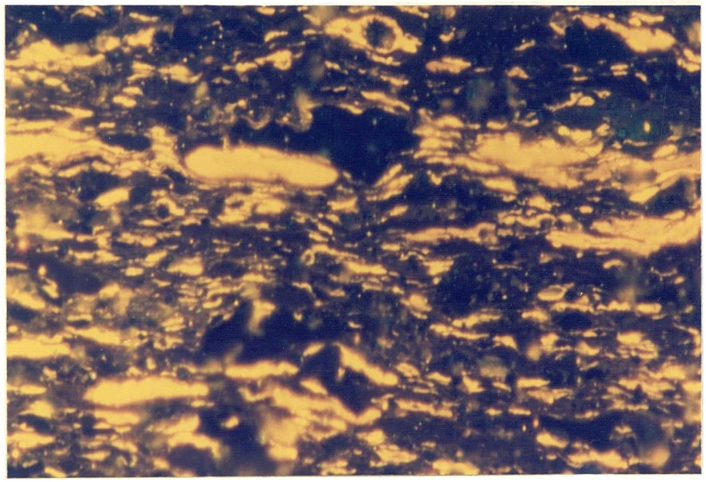


Plate 4.97 Same sample as above, section parallel to bedding (slightly over-exposed): blue-light excitation, oil immersion.

x750

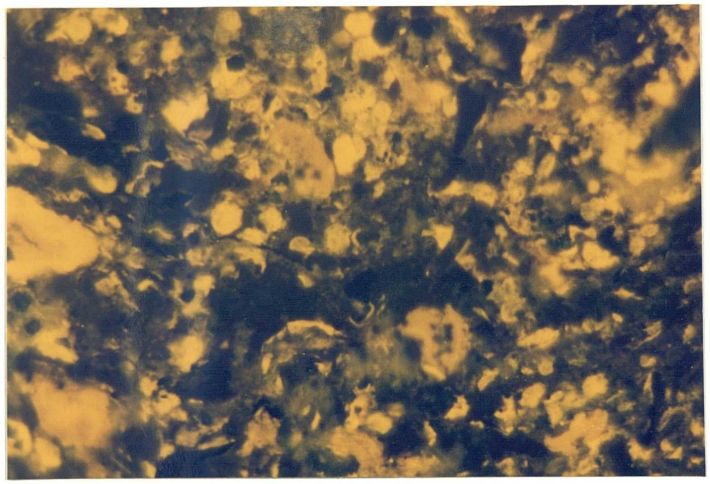


Plate 4.98 *Lingula* shale containing large, thick-walled algal cyst, discrete lamalginite and liptodetrinite: blue-light excitation, oil immersion.

Lingula shale above Top Hosie Limestone, Corrieburn; sample CC 6.

x750

Besides the tasmanitid fragments, the liptinite assemblage in Plates 4.93 and 4.94 also comprises abundant liptodetrinite flecks which may represent the remains of marine phytoplanktonic organisms. The exceptionally intensely-fluorescing flecks at the bottom of Plate 4.93 may constitute comminuted tasmanitid debris. The moderately fluorescing, light orange wisps in Plate 4.94 are very thin-walled microspores and, despite the sample being marine, comprise c.10% of the liptinite assemblage. Another marine assemblage is shown in Plate 4.95. Approximately half of the total organic matter present is represented by intensely-fluorescing, yellow liptodetrinite flecks which, as in other samples analysed, probably represent the remains of marine phytoplankton. The other intensely-fluorescing, elongate entities may be the remains of thin-walled tasmanitids of the type shown in Plate 4.94. All these marine samples display a marked background matrix fluorescence which results in the diffuse appearance of the field of view after several minutes blue-light irradiation.

The intensely-fluorescing thick-walled bodies occurring in the left hand side of the photomicrograph of the marine shale shown in Plate 4.96 may represent tasmanitids of the form shown in Plate 4.93. The discrete lamalginite wisps in this sample are thicker and more robust-looking than those occurring in other marine samples examined so far (compare Plates 4.96 and 4.97 with Plates 4.63 and 4.64), suggesting that they may represent a new algal type.

Another type of algal body not previously encountered in any of the other marine samples previously considered is shown in Plate 4.98. The sample is from a *Lingula* band and, like other *Lingula* bands which are common within the Carboniferous succession in Scotland, is thought to have been deposited under quasi-marine conditions (Forsyth 1980). The algal body appears as a double-walled structure, but this probably results from the compression of what originally may have been a hollow spherical cyst. In addition to the alga described above, the *Lingula* band contains abundant wisps and flecks of the types found in numerous other marine samples.

4.2.4 Fife Coastal Sections

The following sections describe the variation in organic-matter type which occurs within a suite of samples collected from field localities on the Fife coast. Although some of the organic assemblages and types of organic matter present have already been included in earlier sections, consideration of Fife coastal sections is justified on the grounds that, despite these being the most accessible and best-exposed sections of Carboniferous strata in Fife, there is no published information on the type, content and maturity of organic material in these rocks.

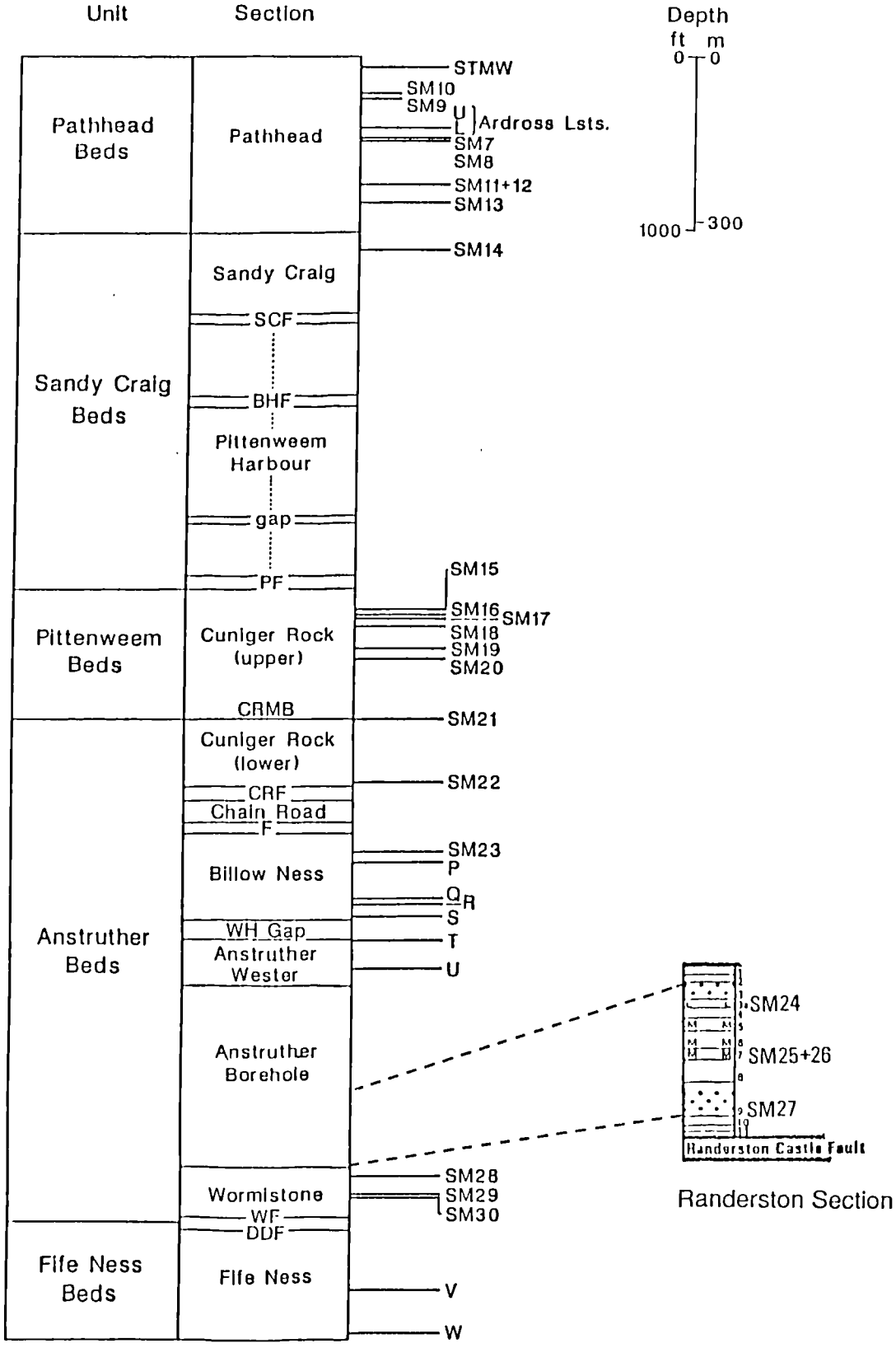
Furthermore, many of the sections exposed along the east Fife coast can be superimposed to give an almost uninterrupted stratigraphic traverse through much of the Calciferous Sandstone Measures (Strathclyde Group) succession, from which it is possible to monitor changes in organic matter input and depositional environments within the sequence. Variation in the maturity of the sediments is discussed in Chapter 5.

In recent years there has been increasing interest in the organic facies present in the Calciferous Sandstone Measures succession on the north side of the Firth of Forth, mainly in response to the discovery of oil shows in the Balfour Anticline of central Fife (see Hallett *et al* 1985 for a review). Although the lacustrine oil shales of the Lothians have long been suspected to be the sources of oil in the Midlothian district, the presence of a deltaic facies over much of Fife, with a lack of any known thick developments of oil shale, has made a specific source-rock horizon difficult to identify. An additional reason for studying the organic matter in the Fife coast sections, therefore, is to provide an insight into possible source-rock horizons within the Lower Carboniferous strata of Fife. A study of the coastal sections is particularly important since much of the inland area of Fife is very poorly exposed. Strata belonging to the Ballagan Formation are not exposed along the east Fife coast, so descriptions of samples taken from onshore boreholes and the type locality at Ballagan Glen are included at the end of the section to complete the analysis of organic matter within the Calciferous Sandstone Measures succession.

4.2.4.1 East Fife

Calciferous Sandstone Measures (Strathclyde Group)

The coast section between Pathhead and Anstruther, the Anstruther Borehole and the sections around Fife Ness together cover the known range of the Calciferous Sandstone Measures in east Fife. The juxtaposed sections and the horizons at which samples were taken are shown in Fig.4.3. Stratigraphic details of the succession are given by Forsyth and Chisholm (1977). All the samples collected were argillaceous sediments or coals. Although the section covering the Sandy Craig Beds near Pathhead was traversed, only one suitable sample could be obtained. Additional samples from the Sandy Craig Beds were collected from the St.Andrews Shore Section (SA4, SA5) and the Kinkell Braes Section (StA10; see Fig.4.4). In addition to the section at Pathhead, the Pathhead Beds are exposed on the coast west of St.Monance to Elie, and numerous samples were taken from this section. The characterisation of organic matter was hampered in many cases by the effects of both intrusive and extrusive igneous activity.



STMW St. Monance White Limestone
F Fault
SCF Sandy Craig Fault
BHF Boat Harbour Fault
PF Pittenweem Fault
CRMB Cuniger Rock Marine Band
CRF Cuniger Rock Fault
WH West Haven
WF Wormistone Fault
DDF Danes Dike Fault

Fig.4.3 Calciferous Sandstone Measures succession in east Fife showing the horizons at which samples were taken (see Appendix for Anstruther Borehole).

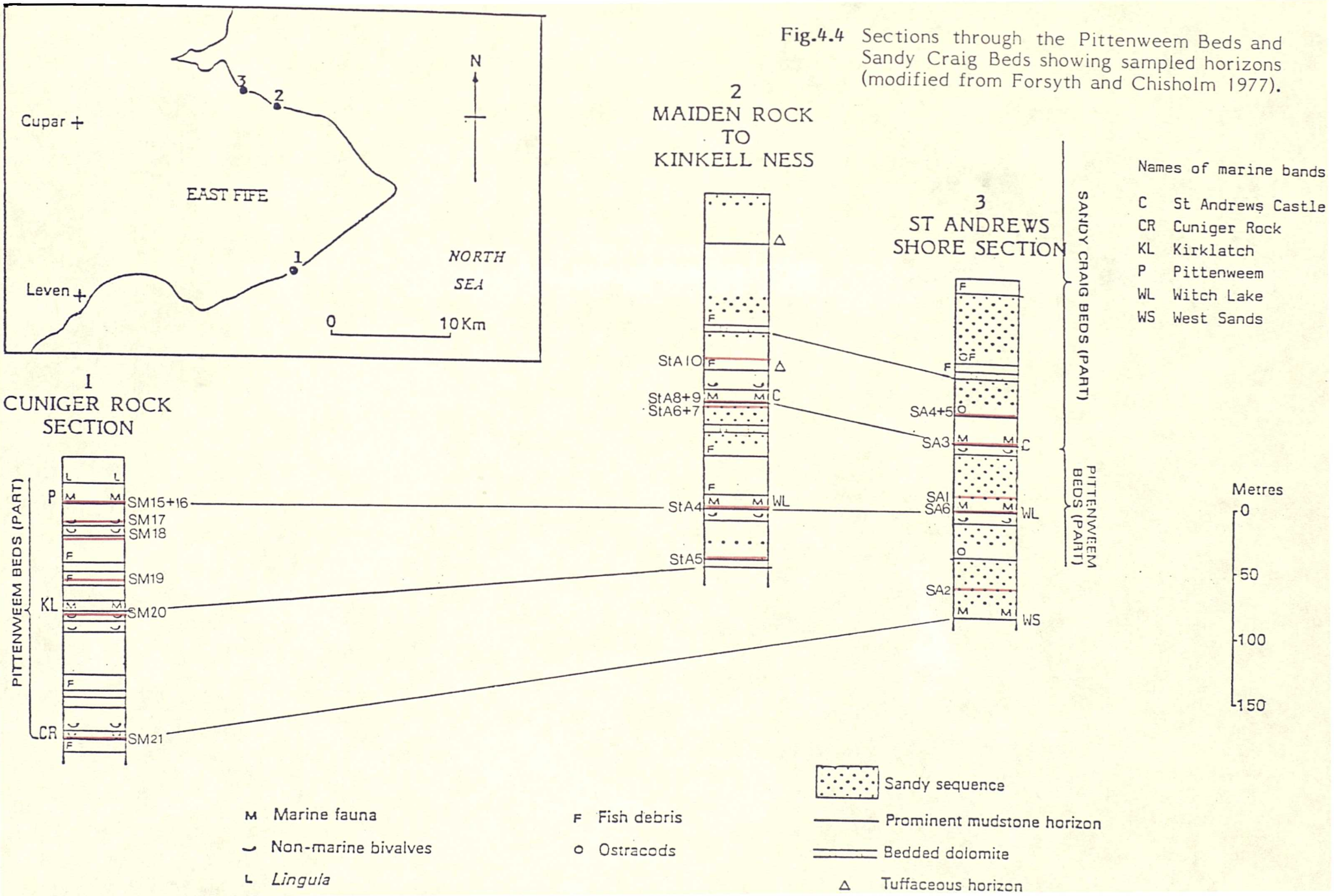


Fig.4.4 Sections through the Pittenweem Beds and Sandy Craig Beds showing sampled horizons (modified from Forsyth and Chisholm 1977).

The lithologies of the argillaceous sediments collected from the Calciferous Sandstone Measures are siltstones and shales, the latter often containing varying amounts of quartz, calcite or pyrite. The organic content of the sediments is generally high, with vitrinite and intertinite comprising most of the organic matter. In contrast to the sediments discussed in previous sections, vitrinite was generally found to be the dominant maceral in the east Fife samples, usually constituting 20-70% of the total organic matter present. A notable feature of many vitrinites within the east Fife Calciferous Sandstone Measures succession is the exudation of a brown humic or bituminous matter from stringers, which imparts a brown stain on the surrounding mineral matrix (Plate 4.99). This observation was most common within samples from the Anstruther Beds, although this may reflect the greater number of samples available for analysis (from the Anstruther Borehole) over this stratigraphic interval.

The content of liptinite varies markedly within the Calciferous Sandstone Measures: it usually represents >10% of the organic content of the sample, but often accounts for *c.*40-70% of the organic matter present. Although no regular trend in maceral composition can be detected throughout the Pathhead to Fife Ness sequence, there are parts of the succession in which the liptinite content of the sediments becomes high, with a significant proportion of the liptinite represented by algal mater. The dominant liptinite maceral throughout the Calciferous Sandstone Measures succession is sporinite, represented mainly by thin-walled microspores. Within the Pathhead and Sandy Craig Beds, sporinite accounts for most of the liptinitic matter in the sediments. The laminated shale below the Lower Ardross Limestone is an exception in that the bulk of the organic matter is represented by discrete lamalginite filaments (sample SM7, discussed in Section 4.2.1.1, and its correlatives *viz.* sample O/SBLA and sample H in the St.Monance to Ardross section). The state of preservation of the sporinite varies considerably: it may be sufficiently well preserved to allow resolution of the exine detail (Plate 4.100) or it may be so severely degraded that it has the appearance of an amorphous "mush" (Plate 4.101) which usually displays variegated fluorescence colours. The fluorescence colour of the degraded sporinite tends to be more orange and the fluorescence intensity much less than that of undegraded sporinite at an equivalent rank as defined by vitrinite reflectance. Many of the samples containing highly degraded spore material are highly pyritic. The pyrite often pseudomorphs liptinitic debris, obscuring any internal morphological details (Plates 4.102 and 4.103).

A change in the constitution of the liptinite assemblage occurs within the Pittenweem Beds exposed in the Cuniger Rock (upper) section, and the change is

Plate 4.99 Bituminous/humic material exuding from vitrinite stringer imparting a dark stain in the mineral matrix: reflected light, oil immersion, plane-polarised light.

Pittenweem Beds, east Fife coast; sample SM 15.

x750

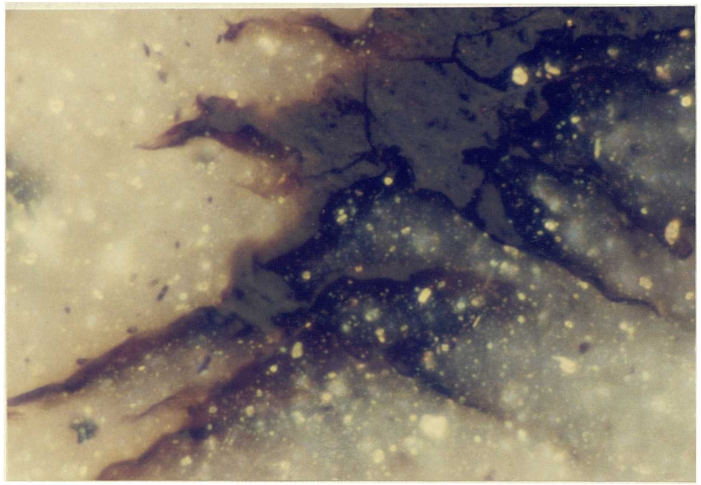


Plate 4.100 Typical state of preservation of sporinite, here shown in a carbargilite. Surface ornament is discernible: blue-light excitation, oil immersion.

Sandy Craig Beds, east Fife coast; sample SM 14.

x750

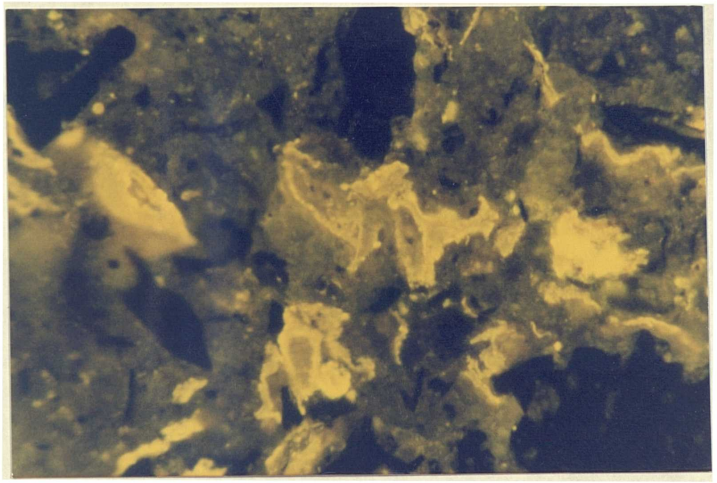
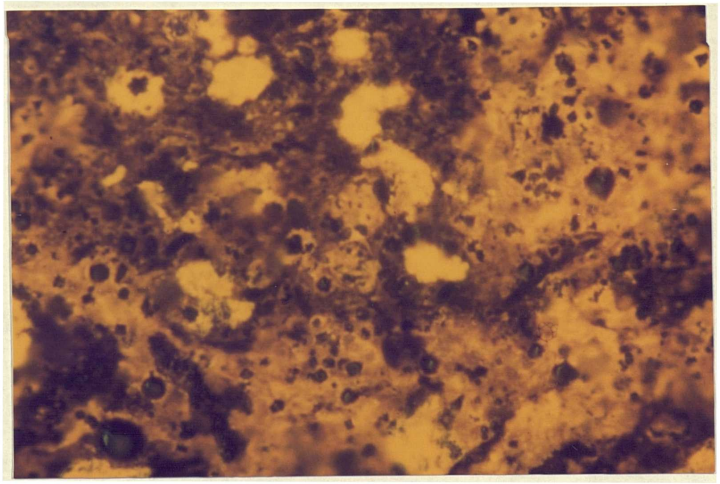


Plate 4.101 Highly degraded, amorphous, spore debris displaying variagated fluorescence colours and varied fluorescence intensities. Yellow blobs are degraded *Botryococcus* fragments: blue-light excitation, oil immersion.

Pathhead Beds, east Fife coast; sample SMW 14.

x750



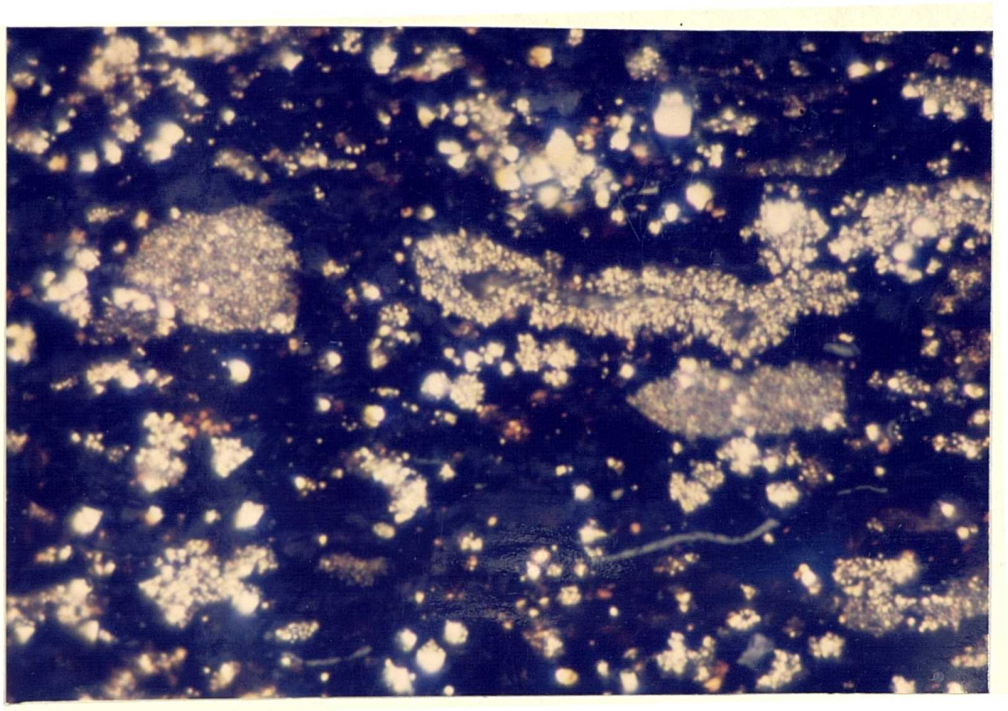


Plate 4.102 Pyrite pseudomorphing liptinite macerals in a shaley cannel coal: reflected light, oil immersion.

Pathhead Beds, east Fife; sample SMW 14.

x750

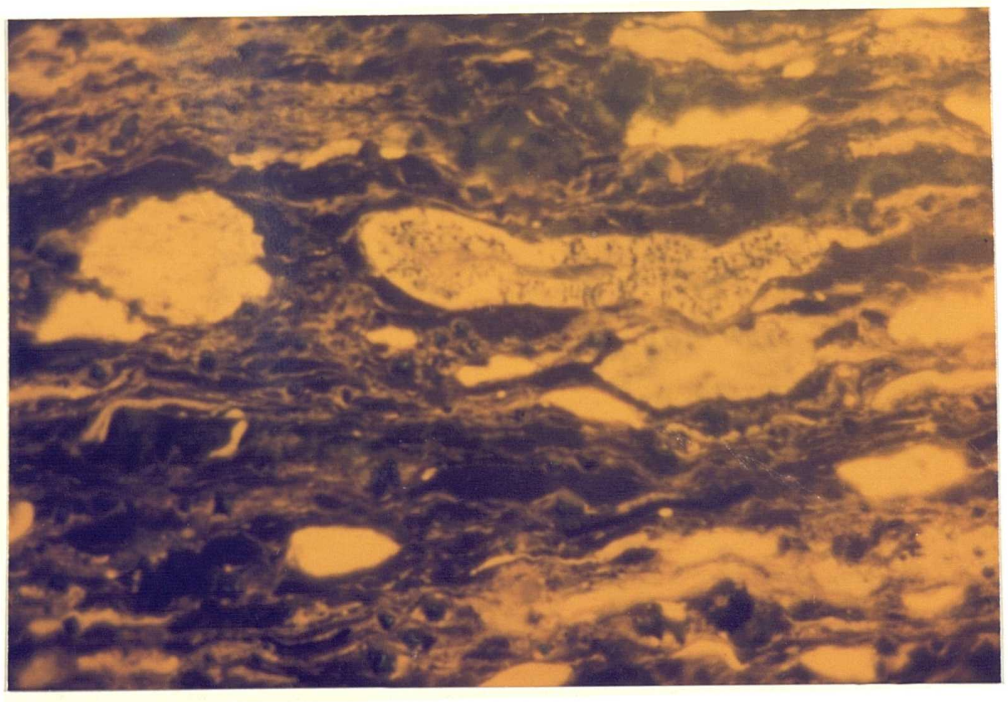


Plate 4.103 Same field of view as above showing degraded sporinite filling most of the matrix, *Botryococcus* (yellow blobs) and a miospore (centre): blue-light excitation, oil immersion.

x750

accompanied by an increase in the amount of liptinite present. The nature of the organic matter in the samples analysed from the section is illustrated in Plates 4.31 and 4.104 to 4.107. Although sporinite is still present throughout the sequence, liptodetrinite flecks (Plate 4.105) and small, discrete lamalginite wisps (Plate 4.31) are prominent constituents, as well as *Botryococcus* remains, the latter only rarely recorded in the Pathhead and Sandy Craig Beds. Although not evident from Plate 4.105, the liptodetrinite in sample SM17 displays an intense, yellow fluorescence suggesting that it is of algal affinity. The stratigraphic position of the sample does not correspond with any known marine horizon and this factor, combined with the relatively low content of vitrinite and inertinite in the sample (Plate 4.104) suggests that the sediment may have accumulated in a lacustrine environment of the type in which the lamosites accumulated, or within a brackish environment. Similar possibilities may be invoked for the deposition of SM18 (Plates 4.30-4.32).

On the basis of the similarity in fluorescence colour and intensity of the liptodetrinite in Plate 4.107 to that of the spores, it is likely that the former was derived from the latter. The organic content of the sample is sufficiently high for it to be classed as a carbargilite.

The amount and type of organic matter of the Pittenweem Beds outcropping in the northern part of east Fife, along the section east of the Rock and Spindle (samples RS25-RS29), are similar to those in the Cuniger Rock (upper) section in that liptodetrinite (probably algal-derived), sporinite and *Botryococcus* are prominent components. In contrast, the liptinite assemblage within the Pittenweem Beds exposed along St.Andrews shore (sample SA2) and along the Kinnkell Braes section (StA6; StA7), east of St.Andrews, consists almost entirely of spore debris.

Several samples from marine bands occurring within the Pittenweem Beds were examined. Those from the Cuniger Rock (upper) section *viz.* the Pittenweem Marine Band (samples SM15, SM16) and the Cuniger Rock Marine Band (SM21), had moderate organic contents of which no more than 10% comprised liptinite, formed of spores and amorphous debris, although some cyst-like structures of the type shown in Plate 4.64 were found in the upper part of the Pittenweem Marine Band. The correlative of the Pittenweem Marine Band in the district around St.Andrews is the Witch Lake Marine Band. Samples of this horizon from the St.Andrews Shore section (SA6) and Kinkell Braes section (StA4) had similar organic contents to the Pittenweem Marine Band, but contained a higher proportion of liptinite (25% in SA6 and 40% in StA4), comprising mainly spores and liptodetrinite wisps, the latter probably of algal origin. Samples of the St.Andrews Castle Marine Band taken from the St.Andrews shore (SA3) and Kinkell

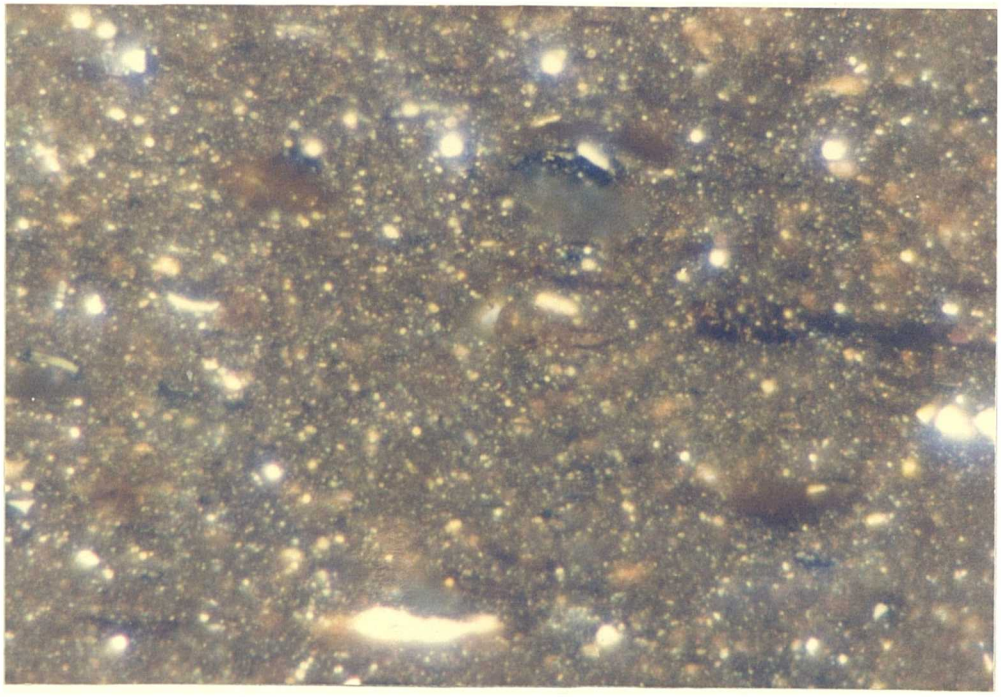


Plate 4.104 Shale from the Cuniger Rock (upper) section; reflected light, oil immersion, plane-polarised light.

Pittenweem Beds, east Fife coast; sample SM 17.

x750

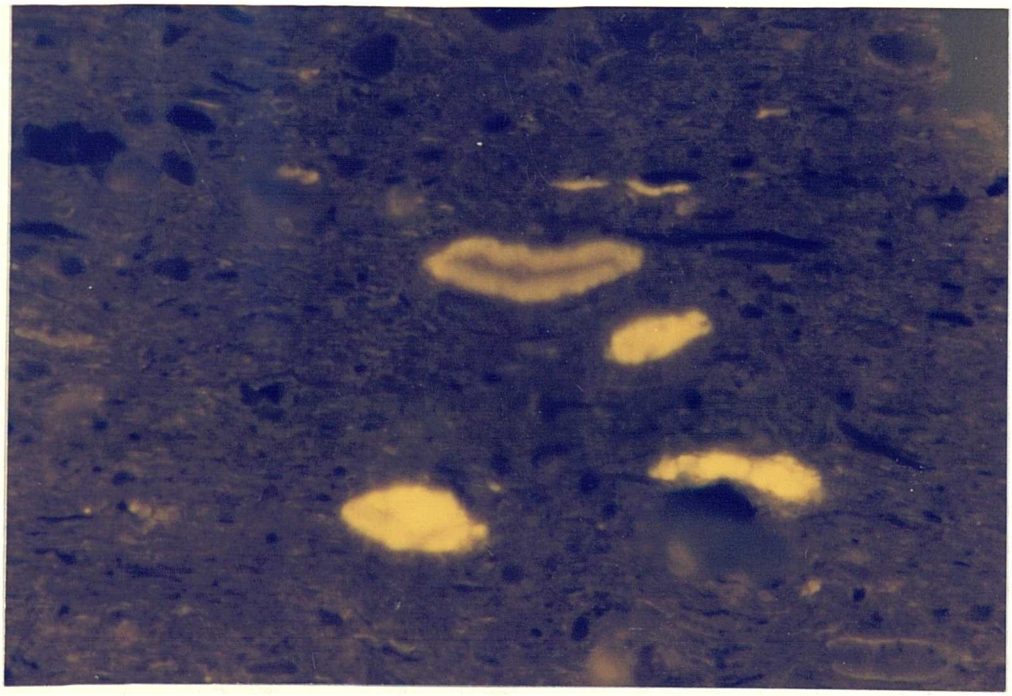


Plate 4.105 Same sample as above showing liptodetrinite filling matrix, spore (lowest fluorescing clast) and degraded *Botryococcus* bodies: blue-light excitation, oil immersion.

x750

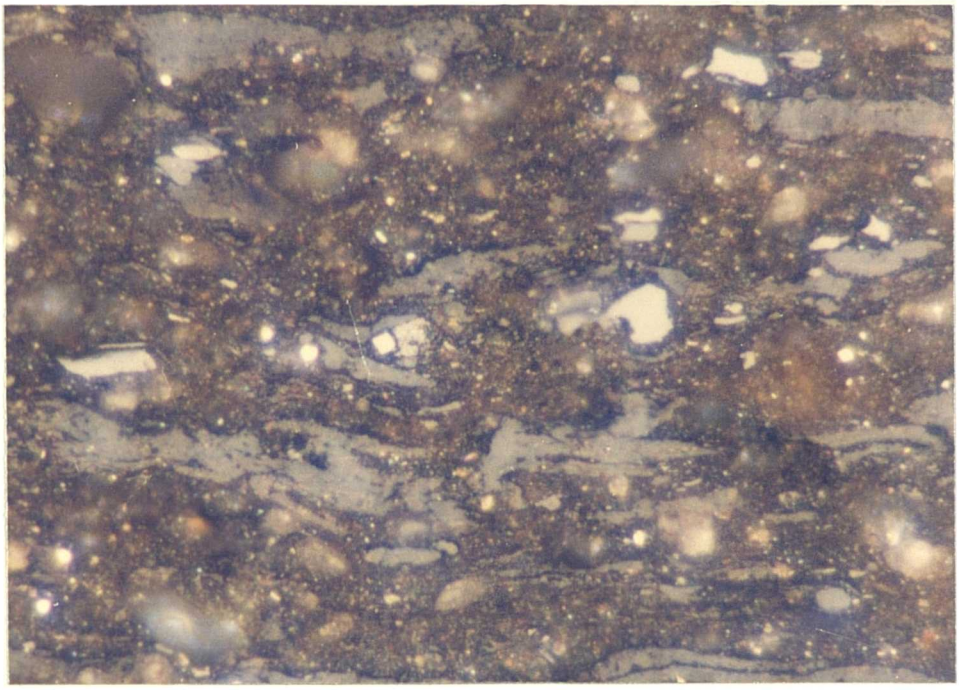


Plate 4.106 Calcareous carbargilite in Cuniger Rock (upper) Section: reflected light, oil immersion, plane-polarised light.

Pittenweem Beds, east Fife coast; sample SM 19.

x750

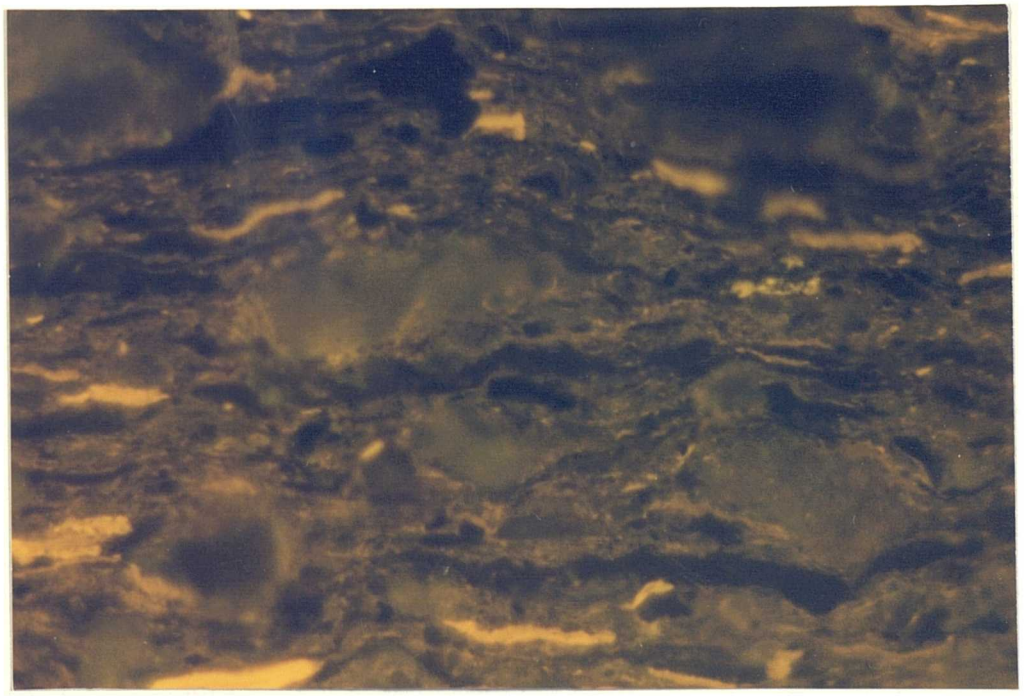


Plate 4.107 Same sample as above showing spores and liptodetrinite: blue-light excitation, oil immersion.

x750

Braes section (StA8 and StA9) all contain spores, but only StA8 and StA9 contain liptodetrinite remains, again probably of algal origin. Although undoubtedly of marine origin on the basis of the presence of marine fossils, the marine bands contain substantial amounts of terrestrial remains, particularly vitrinite and inertinite.

High organic contents with high proportions of liptinite matter continue into the upper part of the Anstruther Beds, i.e. from the Cuniger Rock (lower) section to the Anstruther Wester section (Fig.4.3). Discrete lamalginite wisps and *Botryococcus* remains feature prominently in the liptinite assemblages, particularly in samples from the Billow Ness section. In addition to the algal-rich sediments already described from this part of the sequence in Section 4.2.1 (Psh, Plate 4.33; sample Q Plates 4.31-4.36), sample SM23 (Plate 4.108) is also rich in lamalginite and fits the description of lamosite given in Section 4.2.1.1. The lamalginite in the Billow Ness samples is probably non-marine since the sediments in which it occurs are not known to contain any marine fauna.

The abundance of lamalginite wisps in SM22 (Plates 4.109 and 4.110) gives the sample a marked resemblance to a lacositic coal (Plates 4.55 and 4.56). Because of the larger amount of mineral matter in SM22, the sample can be classed as lacositic carbargilite.

In the lower part of the Anstruther Beds, represented by strata in the Anstruther Borehole and in the Wormistone and Kingsbarns-Randerston field sections, the organic content of the sediments continues to be high, but there is a general reversion to spore-dominated liptinite assemblages. Some samples in the Anstruther Borehole (e.g. SBO7516, SBO7517) do contain large quantities of liptodetrinite flecks (c.40-80% of the total organic matter present). Although none of the shales in the first 550' of the Anstruther Borehole succession is thought to be marine (Forsyth and Chisholm 1968), it is possible that the liptodetrinitic matter of the type seen in samples SBO7516 and SBO7517 could reflect a marine influence because the flecky appearance of the samples when fluorescing is identical to that observed in samples from known marine horizons (e.g. Plate 4.95).

Samples SM24-SM27 were collected from the Randerston Section which, based on lithological and palaeontological resemblance, is thought to correlate with the lower part of the Anstruther Borehole (Forsyth and Chisholm 1968). Although the horizons collected from the Randerston section were not at precisely the same stratigraphic levels as those taken from the Anstruther Borehole, there are general petrological similarities between the two sequences. The lithologies, organic content and bitumen staining of the samples in both suites is variable, as is the composition of the liptinite assemblages, in which sporinite, liptodetrinite

Plate 4.108 Lamosite in the Billow Ness Section: blue-light excitation, oil immersion.

Anstruther Beds, east Fife coast; sample SM 23.

x750

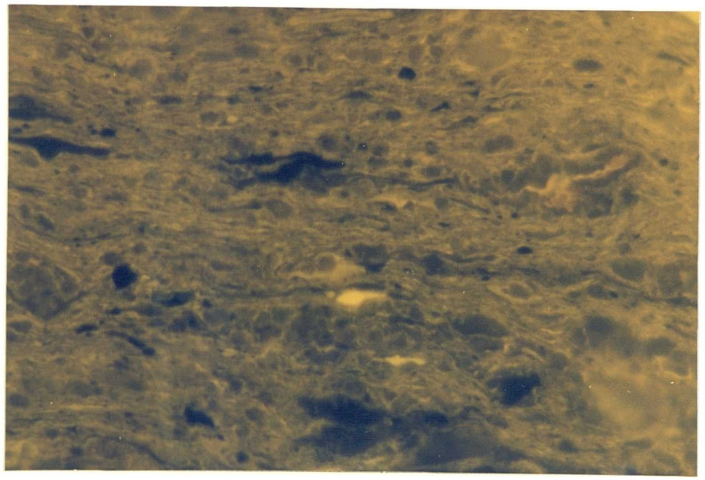


Plate 4.109 Carbargilite in the Billow Ness Section: reflected light, oil immersion, plane-polarised light.

Anstruther Beds, east Fife coast; sample SM 22.

x750

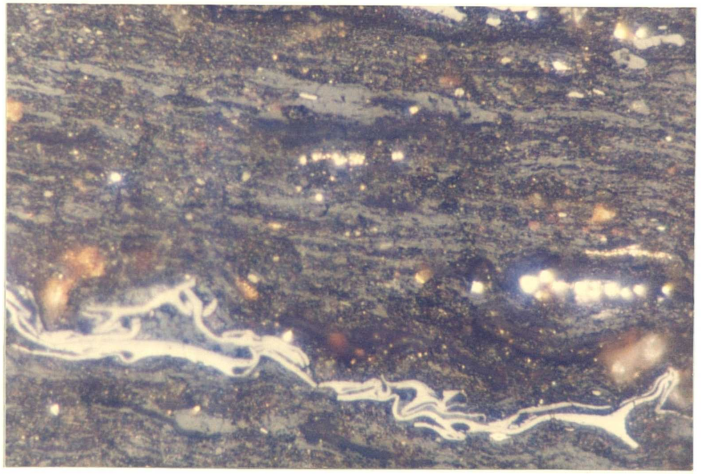
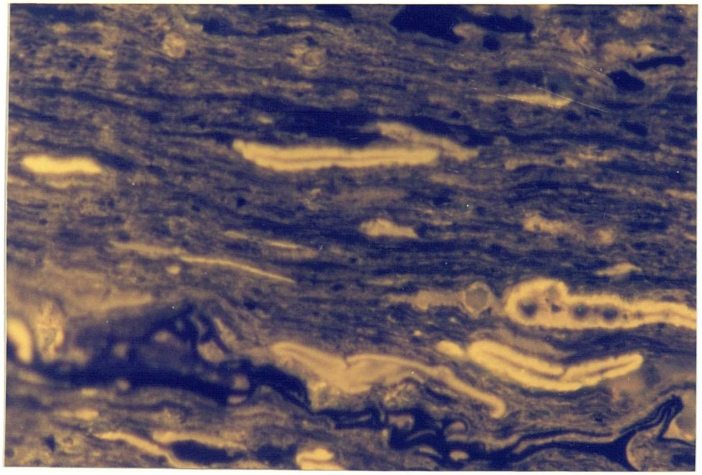


Plate 4.110 Same field of view as above showing lacositic nature of the organic assemblage (cf Plate 4.56): blue-light excitation, air.

x750



and *Botryococcus* occur. Bituminous matter also exudes from vitrinite stringers (cf. Plate 4.99) in samples from both sequences. Given the petrological diversity of other sections of Calciferous Sandstone Measures strata, the similarity between the petrological characteristics in both sequences is not sufficiently distinct to prove (or disprove) the proposed correlation.

Very few samples lying stratigraphically beneath the Anstruther Beds were available for analysis. Of the samples from the Fife Ness Beds, one was of too high a rank to permit maceral resolution, and the other sample (sample V) comprised mainly sporinite (70%) and inertinite (c.30%). Only trace amounts of vitrinite were present.

Samples from the Ballagan Beds in east Fife were obtained from the East Dron and Newburgh boreholes (Browne 1980). The organic content of the samples was generally low and there was virtually no bitumen staining of the mineral matrix. The bulk of the organic matter comprised intertinite particles. Vitrinite was present in only trace amounts, if at all, and liptinite usually constituted no more than 10% of the total organic matter present. The liptinite consisted of fragments of thin-walled spores and discrete cysts of the types shown in Plates 4.111 and 4.112. Flanges and punctae could be discerned on many of the cysts. Long, thin-walled *Tasmanites* were detected in the East Dron borehole (Plate 4.113) and numerous, furrowed cysts of the type shown in Plate 4.114 were observed in the Ballagan Beds in the Newburgh borehole. The high fluorescence intensity of the cysts encountered in the Ballagan Formation suggests that they are probably algal.

Ballagan Formation samples from the Glenrothes borehole (central Fife) and the type locality at Ballagan Glen also contained very little organic matter. Of the samples that had not been severely heat-affected, it was possible to establish that, like the Ballagan Formation samples in east Fife, the organic matter in those further to the west also comprised mainly inertinite. Liptinitic matter was represented mainly by spore fragments and liptodetrinite flecks. No cyst-like bodies of the types described above were noted.

The calcareous nature and low organic content of most of the sediments from the Ballagan Beds examined from the eastern and central Midland Valley would be expected from the proposed depositional environment for this facies *viz.* accumulation of the sediments on a sabkha-like, coastal shelf (Browne 1980). The presence of the marine alga *Tasmanites* is further evidence for a marine depositional environment and suggests that the other cysts are probably also the remains of marine organisms.

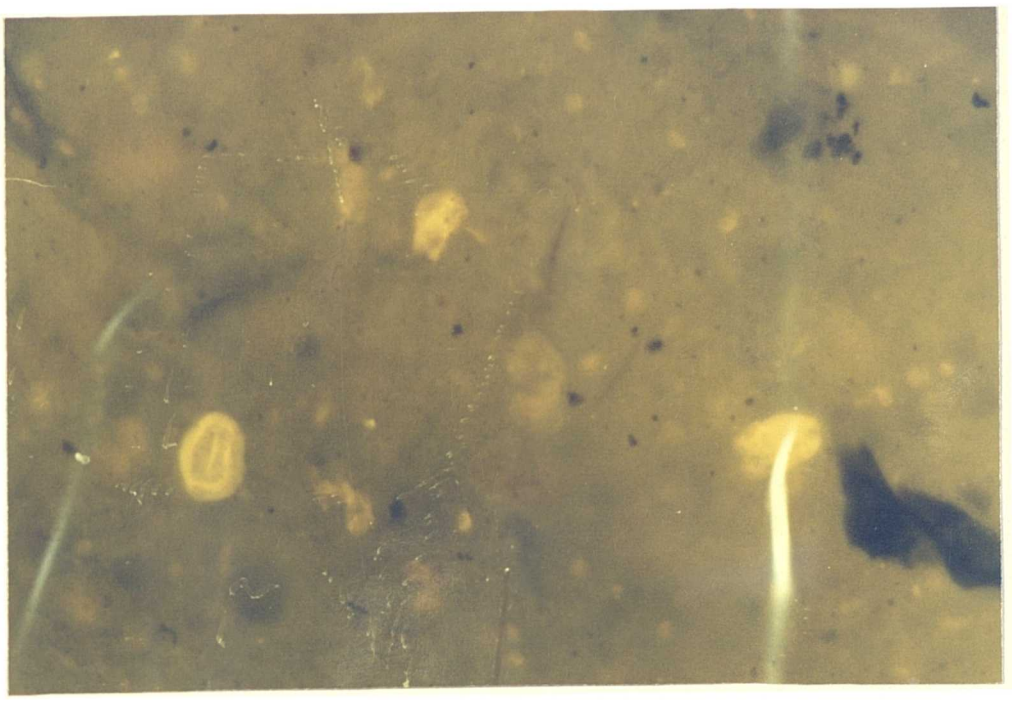


Plate 4.111 Probable algal cysts in Ballagan Beds: blue-light excitation, oil immersion.

Newburgh Borehole, nr Firth of Tay, Fife; sample CS 7.

x750

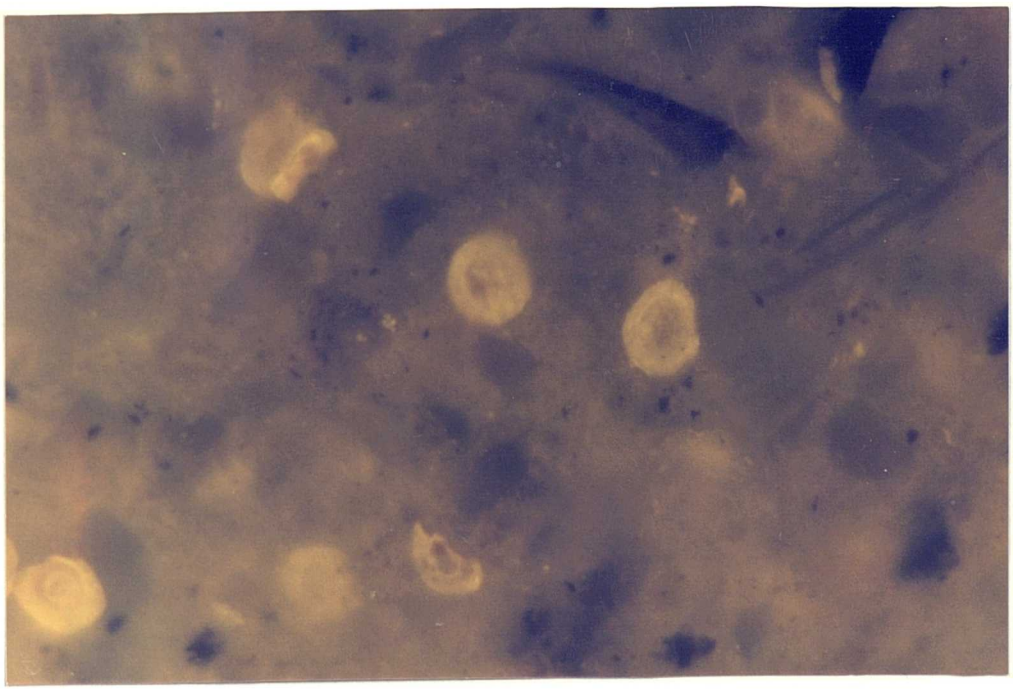


Plate 4.112 Probable algal cysts with prominent peripheral flanges in Ballagan Beds: blue-light excitation, oil immersion (slightly overexposed).

East Dron Borehole, nr Firth of Tay, Fife; sample SBO 9817.

x750

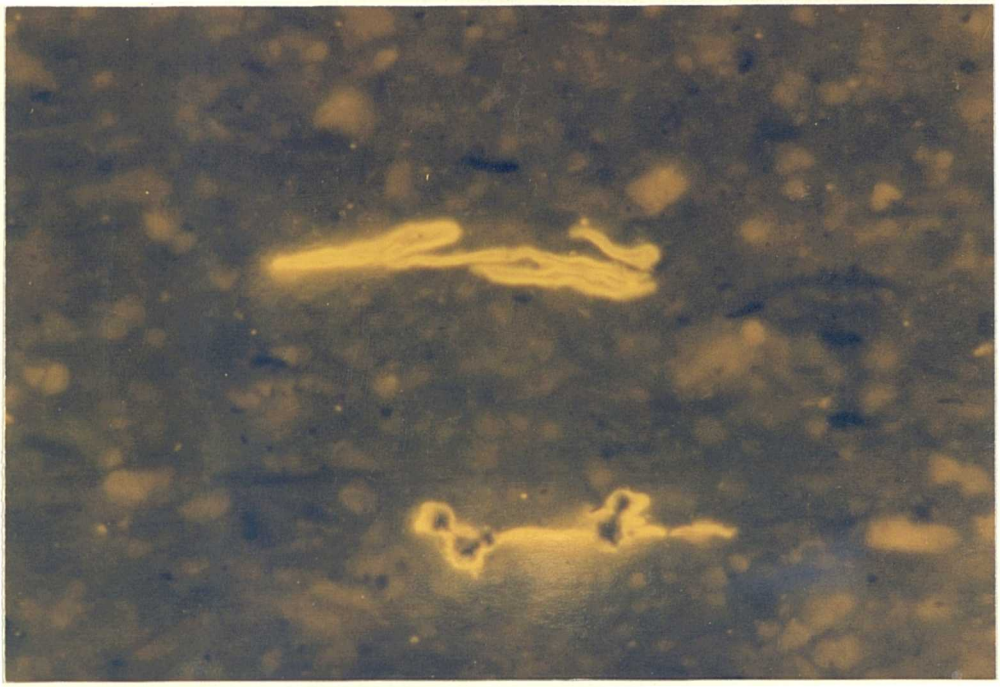


Plate 4.113 Thin-walled *Tasmanites* in Ballagan Beds: blue-light excitation, oil immersion.

East Dron Borehole, nr Firth of Tay, Fife; sample SBO 9817.

x750

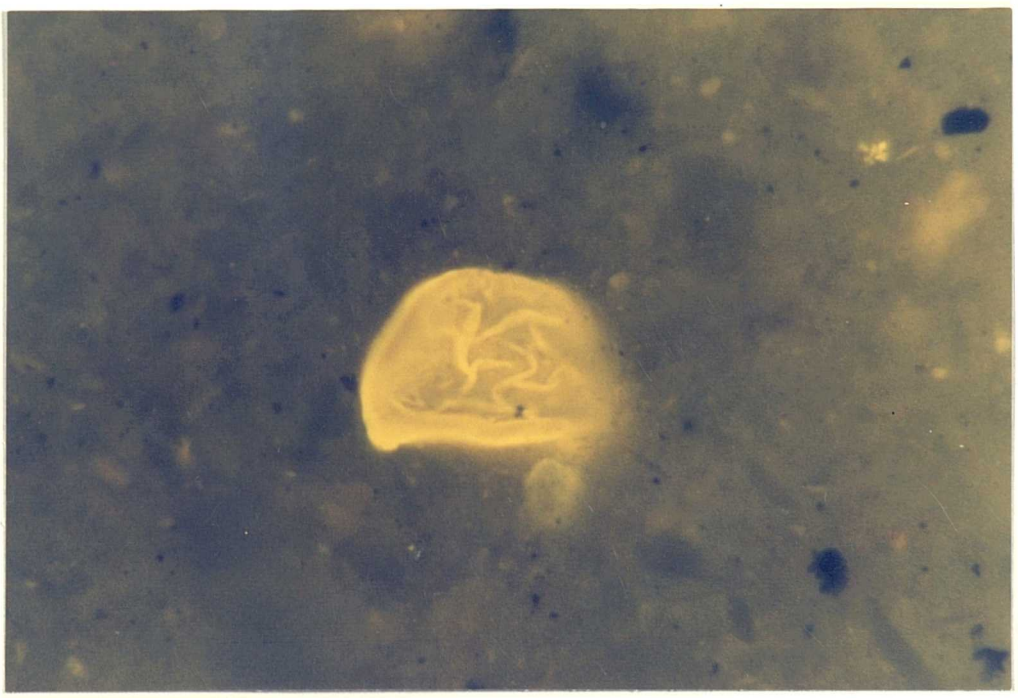


Plate 4.114 Probable algal cyst in Ballagan Beds: blue-light excitation, oil immersion.

Newburgh Borehole, nr Firth of Tay, Fife; sample CS 7.

x750

Lower Limestone Group

All but the topmost beds of the Lower Limestone Group are exposed on the coast at St.Monance where they lie conformably on the Pathhead Beds. Samples SM1-SM6 were sampled from this stratigraphic interval (Fig.4.5). All the shales

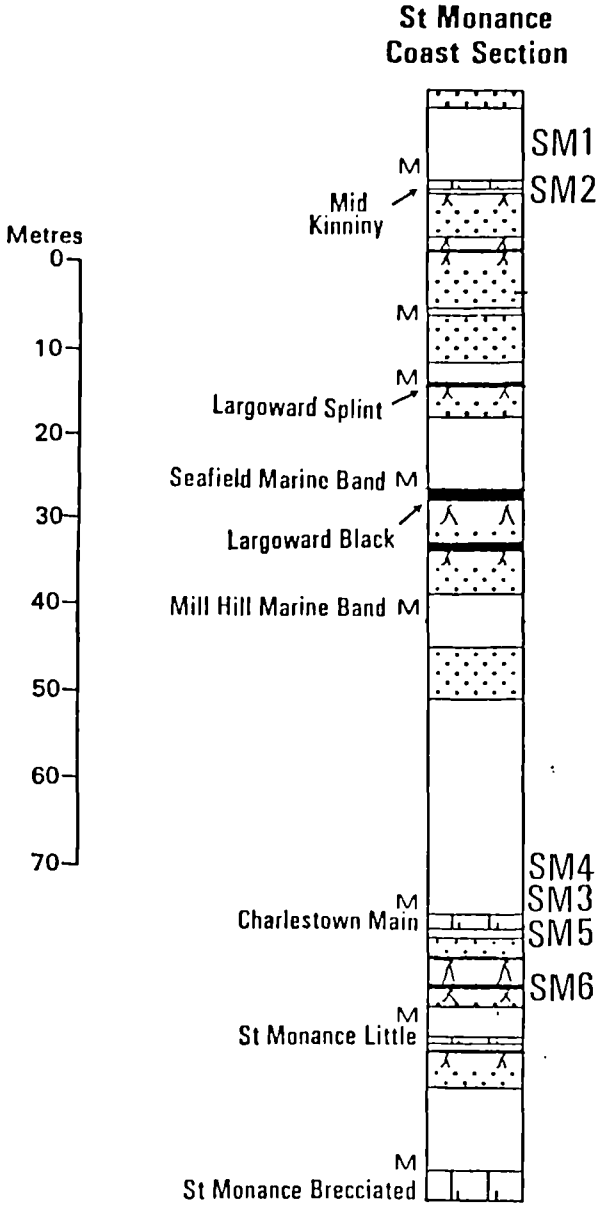


Fig.4.5 Sampled horizons from the Lower Limestone Group succession at St.Monance (modified from Forsyth and Chisholm 1977).

have maceral assemblages dominated by vitrinite and inertinite, with liptinite reaching a maximum of 10% of the total organic content in only the coals (SM2 and SM6) and SM1, a shale from the group of shales overlying the Mid Kinniny Limestone. Fragments of thin-walled microspores are present in all samples. The spores are supplemented by liptodetrinite in marine shales above

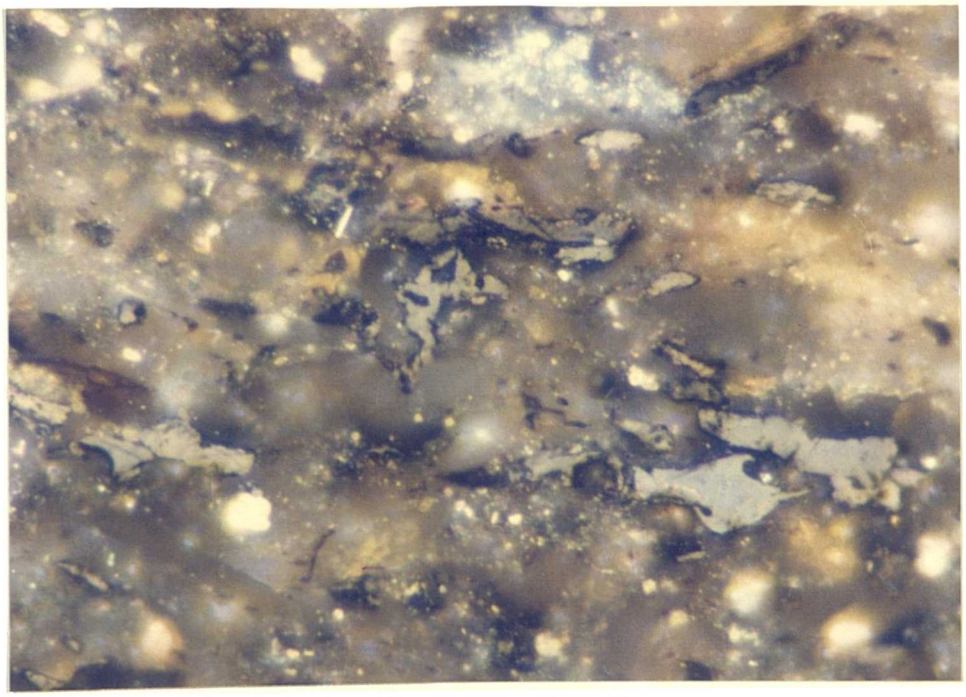


Plate 4.115 Typical field of view of a sediment from the Lower Limestone Group showing virtually no overall staining of the matrix and a terrestrial-dominated maceral assemblage: reflected light, oil immersion, plane-polarised light.

St.Monance Syncline, East Limb; sample SM 4.

x750

the Charlestown Main Limestone (SM3, SM4) and by *Botryococcus* fragments in SM1. The low abundance of liptinitic material in the sediments results in, at most, a very light overall staining of the mineral matrix. A typical field of view of the Lower Limestone Group samples investigated is shown in Plate 4.115.

4.2.4.2 Central Fife

4.2.4.2.1 Kinghorn-Kirkaldy

Calciferous Sandstone Measures

The Pathhead Beds along the coast section between Kinghorn and Kirkaldy are largely replaced by lavas and tuffs of the Burntisland Volcanics. Argillaceous sediments below the First Abden Limestone (=Lower Ardross of east Fife) and below the Second Abden Limestone (=St.Monance Brecciated Limestone of east Fife) were sampled. Marine fossils have been found within both these shale horizons (see Francis 1961 p.21 for details of the succession).

The organic content of the shale below the First Abden Limestone (samples AB1 and AB1.5) is much less than that of the shale below the Second Abden Limestone (sample AB2). The maceral assemblages of both horizons are dominated by inertinitic material. Vitrinite accounts for no more than *c.*10% of the total organic matter present whilst liptinite represents *c.*10-30% of the assemblage. Both horizons contain sporinite which is supplemented by amorphous "blotches" in samples AB1 and AB1.5 and by yellow, wispy liptodetrinite in AB2. All these samples have a dull matrix fluorescence which leads to clouding of the immersion oil after blue-light irradiation. Plates 4.116 and 4.117 illustrate the types of organic matter present in the above samples.

Lower Limestone Group

Spores and wispy liptodetrinite are also prominent components in two liptinite-rich marine shales (c.30%+) sampled from below the Mid Kinniny Limestone (Lower Limestone Group, samples MK1 and MK2). In sample MK2, *Botryococcus* telalginite occurs (Plates 4.118 and 4.119). Only trace quantities of liptinite (sporinite) are found in two (TK1 and TK2) of the four remaining organic-rich samples collected from this field section, these all lying above the Top Kinniny Limestone. Although still dominated by inertinite, these samples contain more vitrinite than those lying below the Mid Kinniny Limestone (MK1 and MK2). Characterisation of the organic matter in the remaining two samples (TK1 and TK2) was not possible since these were severely heat-affected by an overlying quartz-dolerite sill.

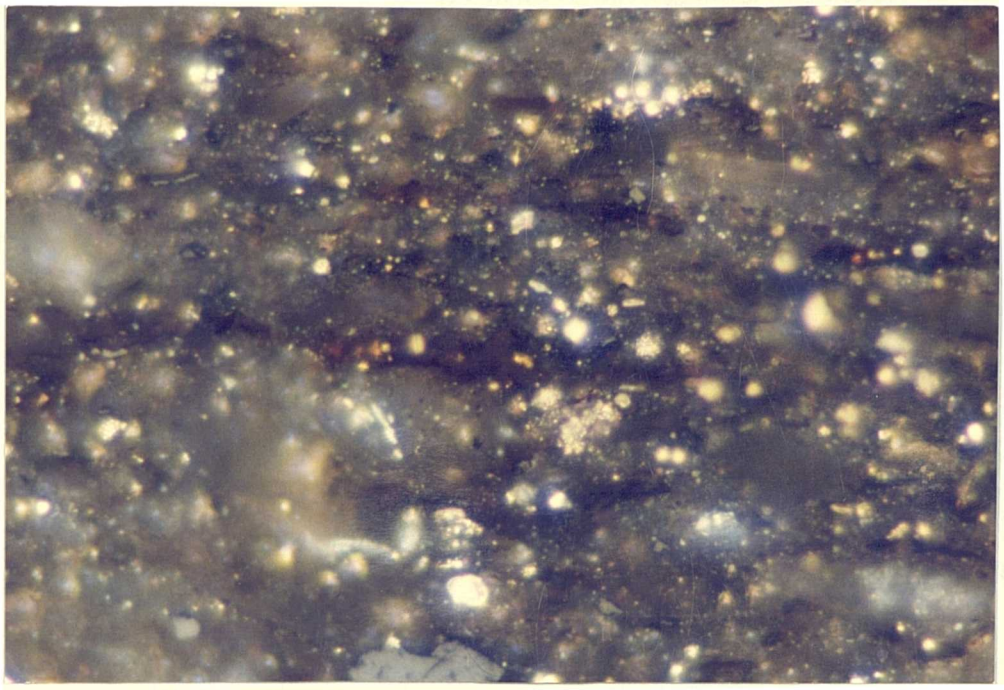


Plate 4.116 Marine shale below the Second Abden Limestone: reflected light, oil immersion, plane-polarised light.

Kinghorn to Kirkaldy coast section; sample AB 2.

x750

Plate 4.117 Same field of view as above showing spore fragments, liptodetrinite wisps and background matrix fluorescence: blue-light excitation, oil immersion.

x750

Plate 4.118 Marine shale below the Mid Kinniny Limestone: reflected light, oil immersion, plane-polarised light.

Kinghorn to Kirkaldy coast section; sample MK 2.

x750

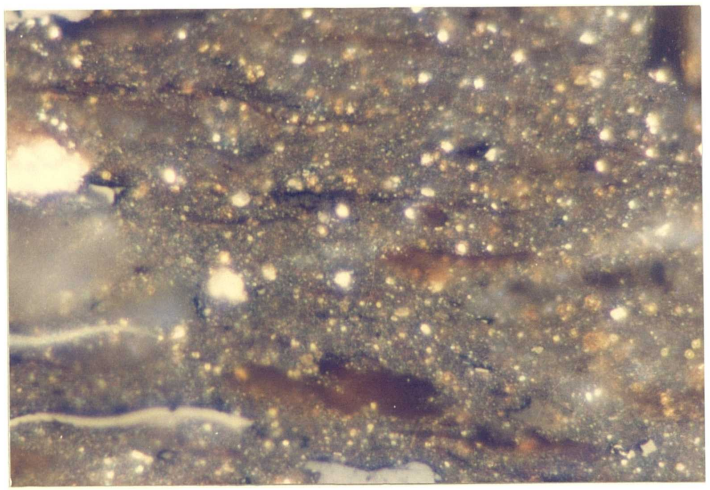


Plate 4.119 Same field of view as above showing spores, liptodetrinite wisps, *Botryococcus* remains (intense yellow fluorescence) and matrix fluorescence: blue-light excitation, oil immersion.

x750

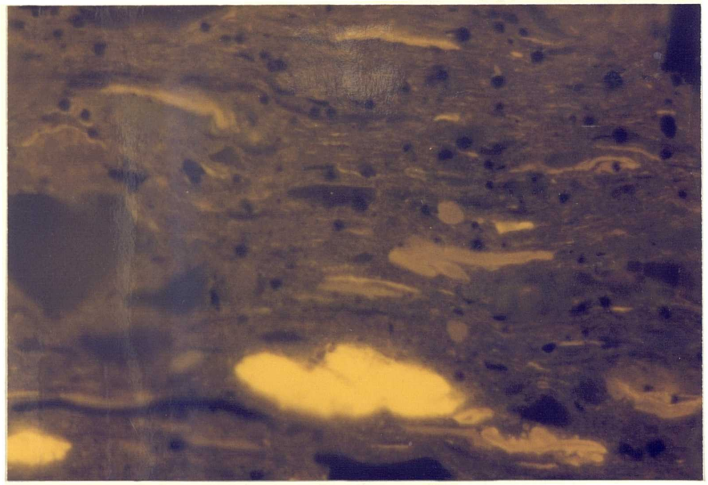
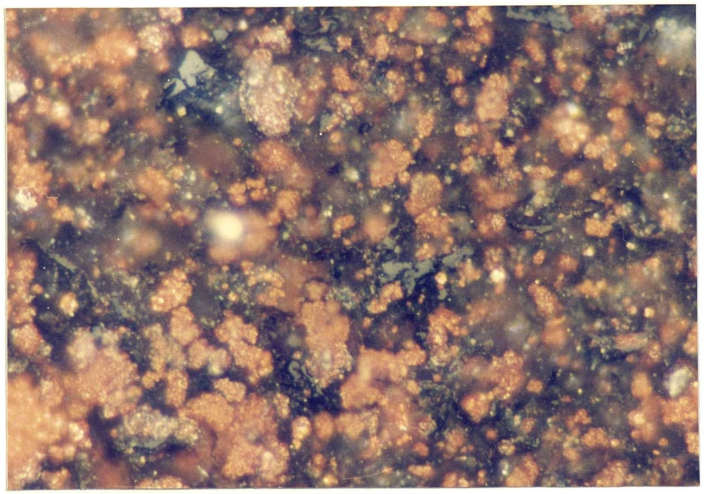


Plate 4.120 Shale below Third Abden Limestone showing severe oxidation of pyrite to haematite: reflected light, oil immersion, plane-polarised light.

Kinghorn to Kirkaldy coast section; sample AB 3.

x750



A sample of particular interest within the Lower Limestone Group of the Kinghorn to Kirkaldy section is the shale below the Third Abden Limestone (=Charlestown Main of east Fife). The shale (AB3) is highly pyritic and contains abundant vitrinite and inertinite. No liptinite was detected, although this lack could be due to the relatively high rank of the sample ($\%R_o$av=1.27). The elevated maturity of AB3 is not thought to be a result of thermal alteration by an underlying teschenite sill (see Chapter 5). The sample is unusual in that the oxidation of pyrite to haematite (Plate 4.120) has been so severe that the sample appears red in hand specimen. Oxidation cracks are also evident in much of the vitrinite. Although present-day weathering can result in the oxidation of organic and mineral matter, the fact that the oxidation is so severe in a sample which, in hand specimen, is highly compact and hard and which, in the field, does not appear to be fissured, suggests that oxidation may have been contemporaneous with, or shortly followed, sediment deposition. The absence of oxidised vitrinite and haematised pyrite in other sediments of the succession (apart from TK2, lying near a quartz-dolerite sill) corroborates this suggestion since weathering in recent geological time might be expected to have affected organic and mineral matter throughout the whole coastal section.

4.2.4.2.2 West Wemyss

Five samples from the Middle Coal Measures were collected from exposures at West Wemyss (samples BP to BSOS in Appendix pp.125-126). All samples were coals or sediments rich in humic materials. Apart from one carbargilite (BSOS), the samples showed reflectance values ($\%R_o$av=0.77-1.21) which, when interpreted in conjunction with those of other samples at the same stratigraphic level (see Queenslie Marine Band map in Chapter 5), have been developed as a consequence of igneous activity.

The reddened shale above the Bush Coal (sample BUSH SH) displays identical petrographic characteristics as sample AB3.